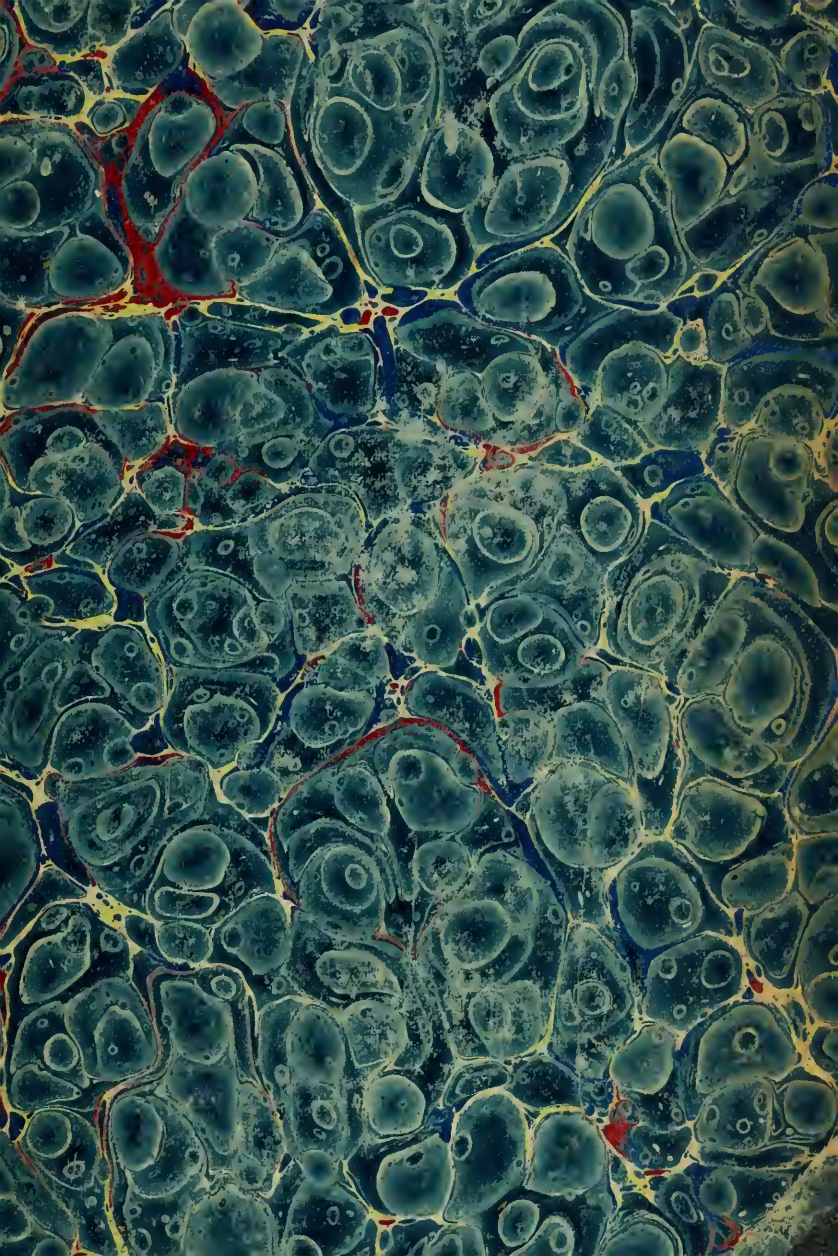

THE ROYAL GARDEN INSTITUTE

REVIEW

—OF—

American Chemical Research

VOL. V. 1899.

Contributed by Members of the Instructing Staff of the Massachusetts Institute of Technology.

ARTHUR A. NOYES, Editor.

HENRY P. TALBOT, Associate Editor.

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TECHNICAL CHEMISTRY	A. H. Gill and F. H. Thorp

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[Contribution from the Massachusetts Institute of Technology.]

REVIEW OF AMERICAN CHEMICAL RESEARCH.

Vol. V. No. 1.

Arthur A. Noyes, Editor; Henry P. Talbot, Associate Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

INORGANIC CHEMISTRY.

Henry Fay, Reviewer.

A Reduction of Permanganic Acid by Manganese Peroxide. By H. N. Morse and C. L. Reese. *Am. Chem. J.*, 20, 521–535.—In a previous paper (*this Rev.*, 2, 85) it was shown that permanganic acid decomposes in presence of manganese dioxide and a reduction of the acid takes place with the liberation of three-fifths of its active oxygen. It was suggested later that this phenomenon might explain the evolution of oxygen which takes place when hydrogen or carbon monoxide is absorbed by a five per cent. acidified solution of potassium permanganate. H. Hirtz and V. Meyer maintained that the phenomenon of the evolution of oxygen observed by Meyer and Von Recklinghausen was fundamentally different from that observed by Morse, Hopkins, and Walker, because the latter experimented only with *neutral* solutions, and the evolution of oxygen which occurs *during the absorption* is much more rapid than that which takes place *after the exhaustion* of the gas. The authors point out that the first objection is invalid; for out of 48 experiments 35 were made with acidified permanganate solution. In regard to the second objection, the suggestion is offered that the rapid initial evolution of oxygen is in some way connected with the nature of the gaseous reducing agent or that the initial peroxide molecules are of greater simplicity. Meyer and von Recklinghausen obtained about 1.9 to 2.9 cc. of oxygen when air was shaken with a five per cent. acidified solution of potassium permanganate which had been previously boiled, and they believed that there was a definite limit to the evolution of oxygen. The authors show that boiling with sulphuric acid produces man-

ganese dioxide, which may be the cause of the decomposition, and that there is a gradual, but continuous, decomposition with continued shaking. Working with three solutions which contained respectively 2.822, 5.644, and 51 milligrams of $KMnO_4$ in each cubic centimeter, and which had been filtered through two layers of asbestos, it was shown that the two weaker solutions suffered no appreciable loss of oxygen when shaken 150 to 300 hours, whether the acid added was equivalent to once or six times the potassium of the permanganate. In the strongest solution there was no appreciable loss of oxygen except when the acid present amounted to three times that of the potassium, and even then after agitating 150 hours was not so large as that observed by Meyer and von Recklinghausen. A series of experiments were made to determine the relative rates of reduction when equal volumes of permanganic acid are agitated, on the one hand with a given volume of hydrogen, and on the other with a quantity of peroxide which is equal to that produced by the absorption of all of the hydrogen. The same three solutions were used and were shaken at times varying from 24 to 300 hours and with acid equivalent to all of the potassium and to three times as much. The experiments show that hydrogen as a reducing agent is much more efficient during the first 24 hours than manganous sulphate with the two stronger solutions. During the period from 24 to 150 hours, the oxide produced by hydrogen acted much more rapidly in the permanganate solution containing 51 milligrams $KMnO_4$ than the oxide produced by the manganous sulphate. In the two more dilute solutions this order is reversed. During the period of shaking, from 150 to 300 hours, the oxide produced by hydrogen was decidedly less active than that from manganese sulphate. In the presence of oxide there seems to be no limit to the reaction until all of the permanganic acid is used up.

On the Metaphosphimic Acids (III). By H. N. Stokes. *Am. Chem. J.*, 20, 740–760.—In two preceding papers (*this Rev.*, 3, 4–7) the author has described trimetaphosphimic and tetrametaphosphimic acids obtained from the corresponding phosphonitrilic chlorides, $P_3N_3Cl_6$ and $P_4N_4Cl_8$. He now prepares and describes the next higher members of this series, the pentametaphosphimic and hexametaphosphimic acids, $P_5N_5(OH)_{10}$ and $P_6N_6(OH)_{12}$, by acting on the chlorides with sodium acetate. It is found that there is a close analogy between this series of acids and the series of methylene ring hydrocarbons, and that with respect to stability, power of forming lactones, and the nature of the decomposition-products, the properties of these acids may be explained by stereochemical considerations analogous to those of von Baeyer on the methylene hydrocarbons and of Wislicenus on the lactones. Assuming that the metaphos-

phimic acids are phosphorus-nitrogen ring compounds, and that the mean angle for an eight-membered ring, which is the most stable condition, is 135°, the properties of the other acids may be deduced from this. From the following table it will be seen that as we ascend in the series there is a very rapid increase of stability to a maximum, followed by a gradual decrease. This is in accordance with the experimental data. $P_5N_5(OH)_{10}$ is less stable than $P_4N_4(OH)_8$, but markedly more stable than $P_3N_3(OH)_6$, corresponding to the difference of only 9° from 135° in one case against 15° in the other.

Ring.	Number of sides.	Mean angle.	Difference from 135°.
PN	2	0°	—135°
P_2N_2	4	90°	— 45°
P_3N_3	6	120°	— 15°
P_4N_4	8	135°	0°
P_5N_5	10	144°	+ 9°
P_6N_6	12	150°	+ 15°
P_7N_7	14	154·3°	+ 19·3°
P_8N_8	16	157·5°	+ 22.5°

The acids containing 1 and 2 atoms of phosphorus are unknown; those containing 3, 4, 5, and 6 atoms of phosphorus have been isolated and exist in two atoms, the lactam form, $(PNO_2H_2)_n$, where n is either 3, 4, 5, or 6, which is formed only in neutral or acid solution and the open chain form $(PNO_2H_2)_n + H_2O$ formed under the influence of alkali. The acid corresponding to the chloronitride, $P_7N_7Cl_{14}$, and possibly those from the higher members, exist only in the open chain form. The higher members of the series break down into the more stable form containing four atoms of phosphorus. Pentametaphosphimic acid breaks down under the influence of mineral acids into tetrametaphosphimic acid, triimidotetraphosphoric acid, diimidotriphosphoric acid, and orthophosphoric acid. The sodium and silver salts of penta- and hexametaphosphimic acids in which the metals replaced one-half of the hydrogen, were prepared. Unsuccessful attempts were made to prepare the amides of the metaphosphimic acids by treating the chloronitrides with strong ammonia.

On the Claims of Davyum to Recognition as a Chemical Element. By J. W. Mallet. *Am. Chem. J.*, 20, 776–783.—Davyum has been described by Kern as having been obtained from platinum ores. He found its atomic weight to be 154, and one of its characteristics was the insoluble double sodium salt. The material investigated by the author was obtained from a London manufacturer of platinum: the filtrate from the aqua regia solution, after decantation from osmiridium and separation of the platinum by means of ammonium chloride, had been evaporated to dryness with sodium chloride. On taking this up in a small quantity of water, the insoluble residue, where davyum

should be found, was proved by the author to be a mixture of finely divided quartz, zircon, and osmiridium. In the precipitation of platinum from certain liquors, ammonium chloride saturated with sodium chloride is used. By evaporation of the filtrate there was formed a buff-colored powder consisting of octahedra. The metal was reduced by pure zinc, dissolved in aqua regia, the sodium double salt again made, dried, weighed, and reduced in hydrogen. Assuming the formula for the double salt to be Na_2MCl_6, the atomic weight of the metal was deduced as 151.5, which agrees closely with Kern's value. The properties of the metal obtained were similar to those described for davyum, but it was shown to consist of iridium and rhodium in about equal amounts and of a trace of iron.

The Formation of Alums by Electrolysis. By Jas. Lewis Howe and E. A. O'Neal. *J. Am. Chem. Soc.*, 20, 759–765.—Solutions of metals in the lower state of oxidation were electrolyzed in a platinum dish, which formed the positive electrode, in presence of sulphuric acid and the different alkali sulphates. The rubidium and caesium iron alums and the rubidium and caesium cobalt alums were prepared in this way.

Derivatives of the Tetrachlorides of Zirconium, Thorium, and Lead. By J. Merritt Matthews. *J. Am. Chem. Soc.*, 20, 815–839.—By bringing together ethereal solutions of the tetrachlorides of zirconium, thorium, and lead, with different substituted ammonias, direct addition takes place. Four molecules of methyl, ethyl, and propyl amines are added to each of the tetrachlorides. Zirconium tetrachloride combines with four molecules both of aniline and toluidine; thorium tetrachloride with four of aniline and three of toluidine; and lead tetrachloride with three of aniline, decomposing toluidine. Two molecules each of pyridine, quinoline, and naphthylamine combine with zirconium tetrachloride, one each with thorium tetrachloride, while lead tetrachloride combines with one of pyridine and naphthylamine, and two of quinoline. Under different conditions eight, six, and two molecules of ammonia add directly to zirconium tetrachloride; eight and six to thorium tetrachloride; and four to lead tetrachloride.

Derivatives of the Tetrabromides of Zirconium and Thorium. By J. Merritt Matthews. *J. Am. Chem. Soc.*, 20, 839–843.—Zirconium tetrabromide adds itself directly to four molecules of ammonia, ethylamine, and aniline, and to three of pyridine; thorium tetrabromide adds directly to one molecule of pyridine, three of ammonia, and four of ethylamine and aniline.

Review and Bibliography of the Metallic Carbides. By J. A. Mathews. *Smithsonian Miscellaneous Collections, No.* 1090, 1–32.

[Contribution from the Massachusetts Institute of Technology.]

REVIEW OF AMERICAN CHEMICAL RESEARCH.

Vol. V. No. 2.

Arthur A. Noyes, Editor; Henry P. Talbot, Associate Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

GENERAL AND PHYSICAL CHEMISTRY.

A. A. Noyes, Reviewer.

New Experiments on the Quantitative Synthesis of Water. By Edward H. Keiser. *Am. Chem. J.*, 20, 733–739.—The apparatus and method employed were as follows: A glass tube 5 ½ cm. in diameter, with a slight constriction two-thirds of the way down, was drawn out at the bottom and fused to a glass stop-cock, and was closed at the top with a ground glass cap provided with a three-way cock. The lower compartment of the tube, below the constriction, was filled with sublimed phosphorus pentoxide. The cap was put on, and the tube was evacuated with a Töpler air-pump and weighed. The cap was then removed, and a cylindrical tube, open above and perforated with a number of small holes near the bottom, filled with palladium sponge prepared by reduction with hydrogen, was inserted in the upper compartment above the pentoxide. The cap was instantly replaced, the tube exhausted, and a second weighing made. Hydrogen, made by electrolyzing dilute sulphuric acid and purified by passing through caustic potash, over heated palladium, to convert any oxygen present to water, and finally through U-tubes containing solid potash and phosphorus pentoxide, was slowly admitted through the three-way cock, until the palladium had become saturated. Then the excess of gas, together with any impurities contained in the total amount absorbed, was pumped out, and a third weighing made. The difference between this and the second weight was the amount of hydrogen converted into water by the next operation. This consisted in admitting very gradually electrolytic oxygen puri-

fied in the same way as the hydrogen. The union with the hydrogen absorbed in the palladium occupied four to five hours, and an excess of oxygen was then allowed to stand in the tube over night. This was then removed by drawing it out at the bottom through the phosphorus pentoxide, and the evacuated apparatus was weighed a fourth time, the difference between the third and fourth weights giving the weight of oxygen that had combined with the hydrogen. Finally, dry air was admitted, the cap was removed, the inner tube with the palladium taken out, the cap replaced, and the apparatus again weighed after evacuation. The difference between this last weight and the first one of all is the weight of water absorbed by the pentoxide. This should check, of course, with the sum of the weights of oxygen and hydrogen, if there is no error from incomplete drying of the gases or leakage. This was found to be very nearly the case in four out of the six experiments that were carried through. The data of these four experiments, which alone are communicated, are as follows :

				At. wt. O (H = 1).	
Wt. of H.	Wt. of O.	Sum of H+O.	Weight of H_2O found.	From H_2:O.	From H_2:H_2O.
0.27549	2.18249	2.45798	2.45975	15.846	15.858
0.27936	2.21896	2.49832	2.49923	15.886	15.892
0.27091	2.15077	2.42168	2.42355	15.880	15.892
0.26845	2.13270	2.40115	2.40269	15.890	15.900
			Mean,	15.874	15.886

The mean of the two averages is 15.880, which is in complete agreement with the value found by Morley and other recent investigators.

On the Cause of the Retention and Release of Gases Occluded by the Oxides of the Metals. By Theodore William Richards. *Am. Chem. J.*, 20, 701–732.—Experiments are first described which show that samples of cupric oxide, prepared by heating cupric nitrate under different conditions, occluded and set free on treatment with acid, after being ignited for from ½ to 20 hours at temperatures varying from 500° to 830°, 0.55–0.70 cc. of gas for each gram of oxide. The amount of gas varies within the limits just stated with the original method used for converting the nitrate to oxide, but is independent in the case of a definite sample of the duration and temperature of the subsequent ignition as long as the temperature does not exceed 830°. Between 870° and 950°, however, most of the gas is gradually expelled, the rapidity depending on the temperature, and only about 0.05 cc. remains after ½ to 2 hours ignition at 950°. Similar experiments with zinc oxide prepared from zinc nitrate showed, on the other hand, that one gram of it retains, after heating for three hours at 660°, 0.37 cc. ; at 750°, 0.22 cc. ; and

at 880°, 0.16 cc. of gas. The amount retained is thus seen to be dependent on the temperature of the ignition, and a special series of experiments showed that it also varies with its duration, and markedly with the method of preparation of the sample of oxide. Zinc oxide prepared from the carbonate contained no gas, and that prepared by heating the nitrate to 280° contained only 0.015 cc., previous to its ignition at higher temperatures. These facts make it clear that the occluded gas arises from the decomposition of a residue of basic nitrate left in the oxides in their preparation at low temperatures. Interesting experiments were also made on the proportions of oxygen and nitrogen in the gas in relation to the temperature and duration of the ignition, and it was found that both with copper and zinc oxide, as well as with magnesium oxide which had been previously investigated, the proportion of oxygen was much less, the higher the temperature and the longer the ignition. For example, the gas obtained by heating zinc oxide at 660° for three hours contained more than 60 per cent. of oxygen, while that from the oxide kept at 880° for the same time contained less than 20 per cent., the absolute amount of nitrogen per gram being nearly the same in the two cases. The oxygen, therefore, escaped much more readily than the nitrogen. In order to explain this phenomenon, which cannot be due to diffusion or transpiration, the author assumes that the oxides are in a state of partial dissociation, and the continual formation and decomposition of oxide molecules enables the oxygen to pass out from within the solid particles. In support of this hypothesis, among other things, he proves that cupric oxide heated to 790° *in a vacuum* evolves nearly pure oxygen.

The Solubility of Salts of Weak Acids in Stronger Acids. By Arthur A. Noyes and David Schwartz. *J. Am. Chem. Soc.*, 20, 742–751.—The authors have determined the solubility of silver benzoate in nitric and chloracetic acid solutions of various strengths, and have developed mathematically the theory of this phenomenon by applying the principles of mass action and electrolytic dissociation. The calculated effect of the acids in increasing the solubility agrees well with that observed.

The Solubility of Acids in Solutions of the Salts of Other Acids. By Arthur A. Noyes and Edward S. Chapin. *J. Am. Chem. Soc.*, 20, 751–756.—The solubility of benzoic acid in sodium acetate and sodium formate solutions of various concentrations was determined. The theory of the effect is the same as in the preceding investigation, and close agreement between the observed and calculated values was found here also.

Benzaldoxime. By Frank K. Cameron. *J. Phys. Chem.*, 2, 409–416.—The author has investigated the equilibrium conditions between the two stereoisomeric forms of benzaldoxime. He concludes that both forms exist in the liquid condition and that their relative concentrations are independent of the temperature. The stable triple point is 27.7° and at this point the mixture contains 94 per cent. of the α modifications. The eutectic point is at 25°–26°, the mixture then containing 91 per cent. of the α compound.

The Isothermal Pressure-Surface in the Case of Two Single Salts and One Double Salt. By F. G. Donnan. *J. Phys. Chem.*, 2, 417–420.

The Molecular Weight of Orthorhomic, Monoclinic, and Plastic Sulphur in Naphthalene and Phosphorus by the Freezing-point Method. By Samuel D. Gloss. *J. Phys. Chem.*, 2, 421–426.—The author concludes from his experiments that there is no difference in the molecular weights of the three forms of sulphur mentioned in the title in either of the two solvents mentioned.

Potassium Chloride in Aqueous Acetone. By J. F. Snell. *J. Phys. Chem.*, 2, 457–491.—The author communicates the results of experiments in which the temperatures were determined at which numerous mixtures of the three substances, water, acetone, and potassium chloride, separated into two layers. These temperatures lie for the most part between 32° and 110°. He found that even at a very much higher temperature (250°–300°) such solutions do not in any case again become homogeneous. He has also determined the temperature of division of various mixtures of water and acetone saturated with potassium chloride, and the solubility at 30° and 40° of this salt in such mixtures. The graphic representation of the equilibrium conditions involved is discussed at length.

Alcohol, Water, and Potassium Nitrate. By Norman Dodge and L. C. Graton. *J. Phys. Chem.*, 2, 498–501.—The authors have determined the temperatures at which various mixtures of water and alcohol containing from 13 to 85 per cent. of the latter separate into two distinct layers when kept saturated with potassium nitrate. These temperatures lie between 80° and 144°. The temperature of separation was found in one case to be 15° lower when an excess of potassium chloride was added at the same time with the excess of potassium nitrate.

NOTE.

Drown's Method of Determining Silicon.[1]—In the July number of this Journal, George Auchy has described a method devised by him, which will effect a more thorough dehydration of the silica than is obtained by the method usually followed. Dr. Dudley[2] called attention to the difficulty of dehydrating in this case at the Troy meeting of this society in 1896.

Without claiming any superiority over Mr. Auchy's method it may be of interest to describe a modification which has been in use in this laboratory for a number of years. It is not original with the author.

The pig iron or steel is weighed into a No. 4 beaker and brought into solution by the usual method as described by Blair. We then add forty cc. of concentrated sulphuric acid and evaporate to fumes on the hot plate. A leather strap about one inch broad and twenty inches long is passed under the lip of the beaker and the ends clasped between the thumb and forefinger. By a slight wrist movement the contents of the beaker are given a rapid rotary movement. The beaker can, in this way, be heated directly in the full flame of the Bunsen burner with perfect safety. Care only must be taken that the contents are kept in continual motion and that sufficient acid is present to cover the glass exposed to the flame. Under these circumstances any lumps are broken up and a thorough contact between the silica and the very hot acid is insured. In many other cases where evaporation to fumes is necessary and the tendency to bump prevents the simple boiling down of the solution, the use of a strap in this way is invaluable. As a rule, it will be found more convenient than the use of the casserole. It is also very convenient in handling hot beakers as it is adaptable to one of any size.

We perhaps run the risk of recounting what may be to some chemists an old story, but, as in our experience we have yet to visit a laboratory in which the strap was used in this way, it is but reasonable to conclude that it has not met with the attention it deserves.

A. C. LANGMUIR.

LABORATORY OF RICKETTS & BANKS,
NEW YORK.

[1] This Journal, 20, 547.

[2] *Ibid.*, 19, 106.

BOOKS RECEIVED.

Commercial Organic Analysis. A treatise on the properties, proximate analytical examination, and modes of assaying the various organic chemicals and products employed in the arts, manufactures, medicines, with concise methods for the detection and determination of their impurities, adulterations, and products of decomposition. By Alfred H. Allen, F.S.C., F.C.S. Third Edition, Illustrated. With revisions and addenda by the author and Henry Leffmann, M.A., M.D. Volume II.—Part I.—Fixed Oils, Fats, Waxes, Glycerol, Nitroglycerin and Nitroglycerin Explosives. Philadelphia: P. Blakiston's Son & Co. 1899. x+371 pp. Price, $3.50.

Fish as Food. By C. F. Langworthy, Ph.D. Farmer's Bulletin, No. 85, U. S. Department of Agriculture, Washington, D. C. 1898. 30 pp.

Grasses, Clovers, Forage, and Economic Crops. By W. R. Dodson and Wm. C. Stubbs. Bulletin No. 53, Second Series, of the Agricultural Experiment Station of Louisiana State University and A. and M. College, Baton Rouge, La. 55 pp. and several plates.

Vinegar Adulteration and the Extent to Which It Exists in the Samples for Sale in North Carolina. Bulletin No. 153, The North Carolina Agricultural Experiment Station, Raleigh, N. C. 8 pp.

The Adulteration of Coffee and Tea Offered for Sale in North Carolina. Bulletin No. 154, The North Carolina Agricultural Experiment Station, Raleigh, N. C. 16 pp.

Electrolysis and Electrosynthesis of Organic Compounds. By Dr. Walther Löb. Authorized Translation by H. W. F. Lorenz, A.M., Ph.D. New York: John Wiley & Sons. 1898. xiii+103 pp. Price, $1.00.

Ninth Annual Report of the Kentucky Agricultural Experiment Station of the State College of Kentucky for the Year 1896, containing also Bulletin No. 61 (Potatoes), Bulletin No. 62 (Strawberries), Bulletin No. 63 (Tobacco), Bulletin No. 64 (Analyses of Commercial Fertilizers), and Bulletin No. 65 (Analyses of Commercial Fertilizers). Kentucky Agricultural Experiment Station, Lexington, Ky. 1898. xliii+114 pp.

An Introductory Course of Quantitative Chemical Analysis, with Explanatory Notes and Stoichiometric Problems. By Henry P. Talbot. Third Edition, Revised and Enlarged. New York: The Macmillan Co. 1899. 153 pp. Price, $1.50.

Lavas and Soils of the Hawaiian Islands. Investigations of the Hawaiian Experiment Station and Laboratories. Walter Maxwell, Director and Chief Chemist. Honolulu: The Hawaiian Sugar Planters' Association. 1898. 186 pp.

Text-book of Medical and Pharmaceutical Chemistry. By Elias H. Bartley, B.S., M.D., Ph.G. Fifth Edition, Revised and Enlarged. Philadelphia: P. Blakiston's Son & Co. 1898. xiv+738 pp., with 96 illustrations. Price, $3.00.

[Contribution from the Massachusetts Institute of Technology.]

REVIEW OF AMERICAN CHEMICAL RESEARCH.

Vol. V. No. 3.

Arthur A. Noyes, Editor; Henry P. Talbot, Associate Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

GENERAL AND PHYSICAL CHEMISTRY.

A. A. Blanchard, Reviewer.

Cyclical Law of the Elements. By Thomas Bayley. *J. Am. Chem. Soc.*, 20, 927–934.—The author discusses Lothar Meyer's curve of atomic weights and atomic volumes, and presents evidence that the sixth loop or cycle embraces elements with atomic weights between that of caesium and that of an unknown alkali metal of atomic weight 223, instead of 170, as Lothar Meyer suggested.

Atomic Volume as a Periodic Function. By Thomas Bayley. *J. Am. Chem. Soc.*, 20, 935–948.—Constructing an atomic volume curve like that of Lothar Meyer, drawing ordinates through the points that mark the transitions from cycle to cycle which occur just before the alkali metals, lithium, sodium, potassium, rubidium, caesium, and the value 223.7, and drawing abscissae at points corresponding to atomic volumes of 30, 60, 90, 120, etc., the author shows that it is possible to draw straight lines through their intersections, which will also pass through the positions of two or more elements, and that there is a remarkable regularity in the properties of the elements located upon these lines. The position and properties of numerous unknown elements in the sixth, seventh, and eighth cycles are also shown by extending the system of lines.

ANALYTICAL CHEMISTRY.

ULTIMATE ANALYSIS.

H. P. Talbot, Reviewer.

I. Metal Separations by Means of Hydrobromic Acid Gas. II. Indium in Tungsten Minerals. By Elizabeth Allen

ATKINSON. *J. Am. Chem. Soc.*, 20, 797–813.—It is shown that there is a marked similarity in the behavior of the metals when placed in an atmosphere of hydrobromic acid to that noted when hydrochloric acid is used. When volatilization of the bromine compounds occurs, however, it is less prompt than that of the chlorides, and certain of the metals, notably lead and cobalt, form oxybromides, while copper forms a cuprous bromide. Silver and cadmium are changed to bromides. Attempted separations of arsenic and iron in an atmosphere of hydrochloric acid as well as one of hydrobromic acid were both unsuccessful. The analysis of wolframite from Zinnwald and from Cornwall, of hübnerite from Colorado, and of scheelite from New Zealand and Bohemia showed the presence of indium only in the first-named mineral. This confirms the views of Hoppe-Seyler (*Ann. Chem.*, 140, 247), that the indium in the specimen of wolframite from Zinnwald was probably present in the zinc blende. Zinc was absent from the other specimens.

IV. On the Separation of Iron from Zirconium and Certain Other Allied Metals. By J. MERRITT MATTHEWS. *J. Am. Chem. Soc.*, 20, 846–858.—Absolute ether, into which dry hydrochloric acid gas is passed, will separate the iron from a mixture of the zirconium and ferric compounds left after the evaporation of an aqueous solution of the chlorides on the water-bath, without dissolving any zirconium. The latter remains as the oxychloride, and the two metals may be quantitatively separated by this procedure. The same method was employed with practical success for the separation of iron from thorium, cerium, titanium, lanthanum, neodymium, and praseodymium.

The Determination of Sulphur in Asphalt. By E. H. HODGSON. *J. Am. Chem. Soc.*, 20, 882–889.—A comparison of the fuming nitric acid (Carius), deflagration, sodium peroxide, and Eschka methods leads the author to the conclusion that the first-named procedure gives the best results, but is long and precarious because of the bursting of the sealed tubes. Of the others, the author prefers the Eschka method.

On the Facilities for Standardizing Chemical Apparatus Afforded by Foreign Governments and Our Own. By LOUIS A. FISCHER. *J. Am. Chem. Soc.*, 20, 912–927.—The paper presents a brief history of the National Office of Standard Weights and Measures, and contains statements of the present facilities for the examination of instruments used by chemists, and the regulations governing this branch of the work of the office. The provisions made by foreign governments for similar purposes are briefly stated. A device for marking flasks for volumetric analysis is described in detail.

Some Errors in the Determination of Nitrogen. By C. G. Hopkins. *J. Am. Chem. Soc.*, 20, 961–965.—In confirmation of Rempel's results (*Ztschr. angew. Chem.*, *1889*, 331), it is found that there is a loss of ammonia if its solution is exposed to the atmosphere during titration, even while dropping from a burette; and, also, that unless the tube from the condenser in the Kjeldahl method reaches to the bottom of the receiver containing the standard acid solution, the ammonia may accumulate in and supersaturate the upper layers, and escape.

W. H. Walker, Reviewer.

Further Separations of Aluminum by Hydrochloric Acid. By Frank Stuart Havens. *Am. J. Sci.*, 156, 45–48.—The method of Gooch and Havens (*this Rev.*, 3, 30) for the separation of aluminum from iron is here extended with little variation to the separation of aluminum from zinc, copper, mercury, or bismuth. After removal of the aluminum, the ether-acid solution is evaporated to dryness and the remaining metal determined by one of the usual methods.

The Iodometric Determination of Molybdenum. By F. A. Gooch and John F. Morton, Jr. *Am. J. Sci.*, 156, 168–175. —In a former article (*this Rev.*, 2, 68), Gooch and Fairbanks pointed out certain inaccuracies in the iodometric determination of molybdenum as proposed by Friedheim and Euler, and recommended modifications by which such inaccuracies might be eliminated. To this criticism Friedheim took exception, and the authors, having carefully repeated the former work, devote the present article to a review of the subject, and give data which fully substantiate previous conclusions.

On the Determination of Manganese as the Pyrophosphate. By F. A. Gooch and Martha Austin. *Am. J. Sci.*, 156, 233–243.—The success of the analytical process by which manganese is determined as pyrophosphate depends upon the conversion of the amorphous trimanganous phosphate, $Mn_3P_2O_8$, which is at first precipitated, into the crystalline ammonium magnesium phosphate, $MnNH_4PO_4$. The conditions under which this change may be most easily and completely brought about have been very thoroughly studied by the authors. They find that a large excess of ammonium chloride is necessary for the transformation, and that the following procedure gives the most satisfactory results: The slightly acid solution, containing in a volume of 200 cc. an amount of manganese not more than enough to make 0.4 gram of pyrophosphate, 20 grams of ammonium chloride, and 5 to 10 cc. of a cold saturated solution of microcosmic salt, is precipitated in the cold by the careful addition of ammonium hydrate in slight excess. On heating, the precipi-

tate quickly becomes silky and crystalline, and may be filtered, washed, and weighed as usual.

Detection of Sulphides, Sulphates, Sulphites, and Thiosulphates in the Presence of Each Other. By P. E. Browning and Earnest Howe. *Am. J. Sci.*, 156, 317–322.—The method of R. G. Smith (*Chem. News*, 72, 39) for the detection of the above-named radicals in the presence of each other has the two serious drawbacks, that the hydrochloric acid necessary to dissolve the barium sulphite and thiosulphate frequently breaks up the thiosulphate with the separation of sulphur, and that a very small precipitate of barium sulphate is difficult to recognize in solutions colored by iodine and bromine. The authors have been able to overcome these difficulties by using the following modifications of the original method: About 0.1 gram of the substance, dissolved in 10 cc. of water, is made slightly alkaline with ammonia or sodium hydroxide, and a little zinc acetate added, precipitating any sulphide present. The filtrate is made slightly acid with acetic acid, and the sulphate present thrown out of solution by means of barium chloride. Iodine is now added to the filtrate free from barium sulphate until the color is permanent, and the excess then removed by a few drops of a stannous chloride solution (to which has been added a little hydrochloric acid to prevent the precipitation of basic tin salts). A precipitation of barium sulphate at this point indicates that a sulphite was originally present. The thiosulphate which has been changed to tetrathionate by the iodine, is now further oxidized to sulphate by means of bromine water, the excess being removed by stannous chloride as before, and its presence is now indicated by a third precipitate of barium sulphate.

The Estimation of Boric Acid. By F. A. Gooch and Louis C. Jones. *Am. J. Sci.*, 157, 34–40.—Owing to the difficulty of obtaining definite conditions for weighing the calcium oxide used to retain and estimate boric acid when distilled with methyl alcohol from an acid solution, numerous substitutes have from time to time been proposed. The experimental data given in the present article show, however, that none of these are superior to calcium oxide if the precautions given in Gooch's original article are followed. A retainer which is much less hygroscopic and in every way suitable, is found by the authors in sodium tungstate which has been fused with a small excess of tungstic acid. It may be used in a manner similar to the other substances with very satisfactory results.

The Standardization of Volumetric Acid and Alkali. By W. A. Puckner. *Pharm. Archives*, 1, 172–184.—The advantages and disadvantages of a number of the substances frequently

used for standardization are discussed, and a large number of experimental data are communicated. The writer, however, "refrains from drawing conclusions."

PROXIMATE ANALYSIS.

A. G. WOODMAN, REVIEWER.

On Acetic Acid as a Substitute for Ethyl Alcohol in Extracting the Active Principles of some Officinal Drugs. BY EDWARD R. SQUIBB. *Am. J. Pharm.*, 71, 1–14.—In order to measure the comparative capacity of alcohol and acetic acid for extracting the active principles of drugs, the author has made parallel extractions of nux vomica, a drug most difficult to extract completely. The results, obtained by the process of repercolation, using siphon percolators, show in general that by the substitution of the acetic acid menstruum for the alcoholic, one-half the cost of grinding, and five-sixths of the cost of menstruum, are saved, an equivalent product being obtained in larger quantity. The acid preparation has a larger proportion of inert extractive matter, but it gives much less precipitation on dilution than the alcoholic, and that which it does give is not liable to carry down alkaloids soluble in an acid solution. After trying various methods in the endeavor to secure a convenient and fairly accurate process of assay for the mixed alkaloids, the following procedure was adopted: 10 grams of nux vomica, ground to pass through a No. 9 sieve, is exhausted with 10 per cent. acetic acid. The percolate is evaporated to dryness on the water-bath and then dissolved in 10 cc. of a mixture of two volumes alcohol (91 per cent.), one volume ammonia water (10 per cent.), and one volume water. The alkaloids are extracted from this solution by a mixture of equal volumes of chloroform (99 per cent.) and ether (96 per cent.). The chloroform extract is evaporated, the soluble alkaloids taken out by warming with 10 cc. decinormal sulphuric acid, and the final solution titrated with decinormal potassium hydrate, using logwood as an indicator.

A Common Error in Recorded Results of Proximate Plant Analysis. BY LYMAN F. KEBLER. *Am. J. Pharm.*, 71, 25–26.—The author calls attention to the error caused by adding the percentage of ash to the percentage of the other constituents instead of estimating it in the dried residue left after the action of the various solvents.

Coumarin and Vanillin, Their Separation, Estimation, and Identification in Commercial Flavoring Extracts. BY WILLIAM H. HESS AND ALBERT B. PRESCOTT. *Pharm. Rev.*, 17,

7–9.—The method for the separation of vanillin and coumarin proposed by the authors, is based on the aldehydic character of vanillin, which is hydroxymethoxybenzoic aldehyde, while coumarin is the anhydride of coumaric (orthohydroxycinnamic) acid. From 25 to 100 grams of the commercial extract are heated at about 80° C. until the alcohol is evaporated, and a solution of lead acetate is added until no more precipitate forms. The filtered solution is extracted with ether, and the vanillin in the ether extract is shaken out with dilute ammonia. The ether solution is then evaporated over sulphuric acid, and the coumarin in the residue is taken up with ligroin, being obtained in crystals melting at 67° C. upon evaporation of the solvent. The ammoniacal solution is made slightly acid and shaken out with ether as before. After evaporation the vanillin is extracted from the residue by boiling ligroin. It gives a pure crystalline product melting at 80°–81° C. This method was found to give satisfactory results.

Emetine Octoiodide and the Extraction and Estimation of Alkaloids Generally. By H. M. Gordin and A. B. Prescott. *Am. J. Pharm.*, 71, 14–21.—In estimating the alkaloids in medicinal drugs, the simplest and best method of obtaining the alkaloidal solution free from foreign matter is that of Lyons (*Manual Pharm. Assaying*, *1886*, 20). By evaporation of the highly volatile solvent used, however, the results are liable to be high; and, in order to avoid this, the authors have worked out a different method of alkaloidal extraction which is in general the same as that proposed by them for the assay of opium (*J. Am. Chem. Soc.*, 20, 724; *this Rev.*, 4, 115). The method was found to give good results with various drugs, with the exception of ipecac root. It was also found that the separate estimation of strychnine and brucine in nux vomica could be conveniently made by the periodide assay method together with a modification of the method of separation proposed by Dunstan and Short (*Am. J. Pharm.*, *1883*, 579). Emetine octoiodide was prepared and analyzed. It was obtained as a dark-brown powder, difficultly soluble in benzol, ether, or chloroform, quite readily soluble in alcohol, and very soluble in a mixture of alcohol and chloroform. It appears to be emetine hydriodide heptaiodide, $C_{28}H_{40}N_2O_5.HI.I_7$, corresponding to the formula for emetine found by Lefort and Wurz (*Ann. chim. phys.* (5), 12, 247).

Comparison of Methods for Estimating Caffeine. By E. F. Ladd. *Am. Chem. J.*, 20, 866–869.—The author has made comparative determinations of the value of four methods for the estimation of caffeine in tea. The methods employed were those of Vite, Peligot, Crosschoff, and Gomberg. The method of

Vite gave a loss of 10 per cent. on pure caffeine, and a loss of as much as 42 per cent. when working with tea. The other three methods gave good results with pure caffeine. The percentages of caffeine found in three samples of tea are given in the following table:

Method.	Congo tea.	Green tea.	Gunpowder tea.
Peligot	0.843	2.061	3.680
Crosschoff	0.919	2.031	3.200
Gomberg	1.542	2.386	3.986

The higher results given by Gomberg's method, together with its simplicity, make it the most desirable method for the rapid determination of caffeine.

Methods for the Determination of Color and the Relation of the Color to the Character of the Water. By Frederick S. Hollis. *J. N. E. Water Works Assoc.*, 13, 94–111.—The author shows by a series of analyses, extending over a year, that in an unpolluted surface water the variations in oxygen consumed, loss on ignition, and albuminoid ammonia, in general, follow the changes in color. Among the methods for the determination of color are described the Tidy colorimeter, the Nessler scale of Leeds, the method based on a comparison of the natural waters with the Lovibond tintometer (erroneously spelled Lovi*bard*), the platinum scale of Hazen, and the special form of colorimeter used at the Experimental Filter Station of the Boston Water Works. A table is given for the conversion of color readings from the Nessler and natural water standard to the platinum standard.

TECHNICAL CHEMISTRY.

F. H. Thorp, Reviewer.

The Influence of Bismuth on Brass and Its Relation to Fire-cracks. By Edwin S. Sperry. *American Machinist*, 21, 690–692.—The author investigated the truth of the maxim common among brass founders that bismuth is injurious in brass. Five experiments were made in which a pure Lake Superior copper was melted and a certain quantity of a definite alloy of copper and bismuth introduced. Pure refined zinc was then added and the brass cast in a mold. It was then rolled cold. The presence or absence of cracks on the edges and surface of the plate was noted. The plate was then annealed and again examined for fire-cracks; if these were not sufficiently deep to prevent further treatment, the plate was again rolled and examined. The amount of bismuth introduced varied from 0.5 per cent. to 0.02 per cent., and in all cases the amount of cracking was proportional to the quantity of bismuth present. Less than 0.02

per cent. bismuth would produce a satisfactory brass. The author believes he has demonstrated that bismuth is a cause of fire-cracks in brass, but it is not commonly present in sufficient quantities to be considered the *only* cause of them. His results in brief are: Bismuth renders brass cold-short, but has less effect than antimony in this respect; it causes fire-cracks, and brass for cold rolling should not contain over 0.01 per cent. of bismuth; it also causes hot-shortness and latent fire-cracks, *i. e.*, lines of inferior cohesion after annealing which develop into cracks when the brass is rolled.

The Variation in the Composition of "Paris Green," with a Scheme for Its Analysis. By Thomas B. Stillman. *Stevens Indicator*, 15, 233–240.—The composition of a pure Paris green is given as an aceto-arsenite of copper containing in per cent. CuO, 31.29; As_2O_3, 58.65; $C_2H_4O_2$, 10.06. Adulteration as such is rare in this country, but many samples show an excessive amount of arsenious acid, and the commercial material fails to give uniform results when used as an insecticide. Foreign samples are often found adulterated with barium sulphate, calcium carbonate, lead chromate, or gypsum; but these may be added to alter the shade when the material is designed for use as a pigment. A simple scheme for the analysis of Paris greens, containing the above impurities, is given.

Producing Illuminating Gas and Coke in By-Product Coke-Ovens. By H. O. Hofman. *Eng. Min. J.*, 66, 428–430; 458–460.—A study of the working of ten Semet-Solvay coke-ovens at Halifax, N. S., was made by the author. Since 1897 these ovens have supplied 18 candle-power gas to the city for illuminating purposes, while a fuel gas of $8\frac{1}{2}$ candle-power is also obtained. Of the gas made, 32.26 per cent. is illuminating gas and 67.74 per cent. fuel gas; the latter is used to heat the retorts, and 54.84 per cent. of the total gas made is thus utilized; the remainder is sold for heating gas. Every 24 hours 37 tons (of 2,000 lbs.) are coked and yield 310,000 cubic feet of gas, while 75 per cent. of the weight of the coal charged is obtained as coke. Each ton of coal also yields about 5 lbs. of ammonia gas and 12 gallons of tar (120 lbs.). An abstract of a report on an Otto-Hoffmann oven, worked at Glassport, Pa., is also included. The coal used was a washed slack from the Dominion Coal Co., Cape Breton. With an average charge of 14591 lbs. of coal containing 9.9 per cent. moisture, the time of coking was 33 hours and 56 minutes. The yield of products per long ton of coal was: coke, 1593.4 lbs. (71.13 per cent.); tar, 75.7 lbs. (3.38 per cent.); ammonia 7.6 lbs. (0.34 per cent.); gas, 10,390 cu. ft. (16.43 per cent.). Of the gas 49.5 per cent. was

of 14.7 candle-power, and 50.5 per cent. of 9 candle-power, only available as fuel gas. Carbon disulphide, hydrogen sulphide, gas liquor, and loss, amounted to 8.72 per cent. Numerous tables of analyses of the products and calculations of the heating value of the gas, coal, and coke are given. It is determined that 10.9 per cent. of the calorific value of the coal is consumed in the coking operation. It is shown that the production of illuminating and fuel gas and coke in these ovens rests on a sound theoretical and economic basis.

The Le Sueur Process for the Electrolytic Production of Sodium Hydroxide and Chlorine. By CHAS. L. PARSONS. *J. Am. Chem. Soc.*, 20, 868–878.—A short history of the original process is given in which it is shown that some of the criticisms made by Lunge and others are unfounded. A detailed description of the process as carried on at Rumford Falls, Me., follows, in which it appears that the original apparatus has been greatly modified, although the essential features of the process are said to be unaltered. The chief difficulty has always been the diffusion of the caustic solution into the anode compartment. This is combatted by adding hydrochloric acid to the anode compartment, thus decomposing any hypochlorite formed. The amount of acid required is, by the table given, somewhat less than one-sixth of the total weight of salt decomposed. A sketch and a description of the improved cell are given, together with a discussion of the practical working and cost of the process.

Sulphuric Acid and the By-products from Iron Pyrites. By R. G. EWER. *J. Assoc. Eng. Soc.*, 21, 160–171.—After a historical sketch of the sulphuric acid industry, tracing the improvements down to the present, the author describes a modern plant, showing a plan and details of a set of chambers of his own design. The process described shows the working of Spanish pyrites, with recovery of copper, silver, and gold and utilization of the iron oxides by blast-furnaces.

Turf Briquettes in Germany. By JOHN E. KEHL. *U. S. Consular Rep.*, 59, 98.—The preparation of this new fuel is described briefly, and the success of the new venture predicted. The turf (peat) is carried directly from the bog to a breaker from which it goes to a steam dryer, and is thus obtained as a fine dry dust. This is heavily pressed to form briquettes, which furnish a cheap, clean, and easily handled fuel.

Refining Petroleum with Silicate of Sodium. By R. P. ROTHWELL. *Eng. Min. J.*, 66, 338.—This article is in the main a condensed statement of the proposition of J. R. Michler to substitute sodium silicate solution for caustic soda in neutralizing the excess of acid left in heavy petroleum oils after the re-

moval of the acid tar. The separation of the silicic acid is claimed to decolorize the oil, as well as to cause the sludge to settle quickly.

Colored Glazes. By S. Geysbeck. *Brick*, 9, 66.—This is a popular article in which is explained the causes of "crazing" and "shivering" in glazes for pottery. Methods of modifying the glazes to overcome these difficulties are given.

Analyses of Commercial Fertilizers. *Agr. Expt. Sta. Bull. Me., No.* 38; *N. J., No.* 124; *Ark., No.* 47; *Wis., No.* 66; *N. Y., No.* 129; *Md., No.* 52; *Miss., No.* 48; *W. Va., No.* 51; *Conn. 21st Ann. Rep., Pt. II; Cal. Ann. Rep., 1895–1897; Wis. 15th Ann. Rep.*; *W. Va. Special Bull., May 1, 1898.*

Crude Caustic Soda Sold in the Market as Caustic Potash. By Carl E. Smith. *Am. J. Pharm.*, 70, 392–398.—In the course of an investigation of the purity of commercial caustic potash, the author found five samples that were nothing else than caustic soda. It is supposed that they represent the supply furnished to grocers and other consumers who are not expected to test their purchases. The products were of good appearance, and might easily deceive their purchasers. Simple methods of testing crude alkali for sodium and potassium, and also quantitative methods for estimating soda and potash, caustic and carbonate, chlorides, sulphates, and silica in crude alkali, are given. The sensitiveness of sodium cobaltic nitrite as a test for potassium was also determined. A solution containing 0.2 per cent. of potassium hydrate showed turbidity in four minutes, but a weaker solution failed to react after many hours.

Sodium Aluminate as a Means for the Removal of Lime and Suspended Matter from Water for Use in Boilers. By Chas. F. Mabery and Edwin B. Baltzley. *J. Am. Chem. Soc.*, 21, 23–27.—The authors first studied a method of making sodium aluminate, which consisted in adding sodium hydroxide to aluminum sulphate solution of known strength. The solution of sodium aluminate so formed was then added in definite quantity to the water to be purified. The reactions involved in the precipitation are :

$$CaH_2(CO_3)_2+Al_2O_4Na_2+H_2O=CaCO_3+2Al(OH)_3+Na_2CO_3,$$

and

$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4.$$

Seven different waters were tested by this method and also by sodium hydroxide alone, but in each case the latter removed only about one-half the quantity of lime that was thrown ont by the aluminate. The precipitated alumina also removed suspended matter most completely.

Theory and Practice of Asphalt Mixtures. By A. W. Dow. *Am. Gas-Light J.*, 69, 862–863.—In testing asphalt for paving, it is often true that the investigator overlooks the physical laws involved, especially those relating to the attraction and adhesion of liquids to solids. Asphalt cement is properly a liquid, and the author showed by a simple experiment that one used in a Washington pavement flowed perceptibly at temperatures of 26°, 75°, and 140° F. A smooth block of asphalt was placed directly over a small hole in a board, and kept at these temperatures for some time. The amount of flow of the asphalt into the hole was measured. The hardness of a pavement mixture is largely dependent on the character of the sand used, very fine, sharp sand forming a much harder mass than coarse sand whose grains were rounded. With rounded grains it was found possible to make a very soft pavement mixture from asphalt which yielded a very hard mass with sharp sand.

Tanning Leather with the Aid of Electrolysis. By Chas. F. Mabery and K. L. Landgrebe. *Proc. Am. Assoc. Adv. Sci.*, *1898; Abstract Leather Manufacturer*, 9, 138–139.—Early attempts to apply electric currents to tanning date back to 1849 and 1883. The purpose of this investigation was to study the influence of the current on the chemical change and in hastening the process. The action of sodium sulphide as a depilatory was also studied. Samples of sheep, calf, and steer hides were treated in a bath made by mixing one liter of sodium sulphide solution containing 50 grams of the salt with four liters of lime water. After twenty minutes' agitation, the strongly alkaline bath reduced the hair to a pulp, which was easily scraped off, leaving the skin, after washing, ready for the tan. No bate was necessary, and the skin was soft and plump. This prepared skin was placed in a bark extract liquor between carbon plates and subjected to currents varying from three to six amperes, the potential difference varying from six to twelve volts, according to the strength of the tannin solution. A current of air was blown into the bath for agitation. A solution of 240 grams oak extract in three liters of water, with a current of 3.5 amperes (six volts potential), tanned the skin samples completely in 1.5 days. A similar experiment without electricity required six days to tan the skins. The current is supposed to assist in the intimate contact between the inner hide substance and oxygen, and also in precipitating coloring-matter, leaving only a clear tannin solution to permeate the skin. The determination of nitrogen in the hide substance shows that the hydrogen liberated exerts some action on the nitrogenous bodies, probably forming ammonia. The proportion of nitrogen in dry and fat-free hide from the same animals is constant; hence this enables

the proportion of tannin taken up by the hide substance to be calculated. A table of nitrogen determinations in sheep and calf skins, with and without electrical tannage, is given, showing that nitrogen is removed in the electric bath.

BIOLOGICAL CHEMISTRY.

A. G. WOODMAN, REVIEWER.

A Chemico-Physiological Study of Certain Derivatives of the Proteids. By R. H. CHITTENDEN, LAFAYETTE B. MENDEL, AND YANDELL HENDERSON. *Am. J. Phys.*, 2, 142–181.—In the first part of their paper the authors have recorded the results of a study of the physiological effect of a number of cleavage products of proteids, observations having been made as to their influence on blood pressure, on blood coagulation, on lymph flow, flow of urine, and on the apparent immunity conferred upon animals by an intravenous injection of propeptone against subsequent injections of the same substance. The second part of the paper is devoted to a description of the method of preparation of the proteid derivatives used and to a presentation of analyses of (1) antipeptone, which was formed by the action of trypsin on pure antialbumid and was dried at 110° C.; (2) of deuterogelatose, formed by the action of trypsin on gelatine and dried at 105° C. to constant weight; and (3) of the gelatine-peptone separated from the deuterogelatose by ammonium sulphate.

The Effect of Aqueous Solutions upon the Germination of Fungus Spores. By F. L. STEVENS. *Botanical Gazette*, 26, 377–406.—In order to determine the strengths of various solutions which just suffice to prevent the growth of fungus spores, the author has made cultures of various fungi in salt solutions of varying degrees of dilution, using the van Tieghem hanging-drop method. Of the salts used, mercuric chloride had the most marked toxic effect, while potassium cyanide was remarkably weak, although it was found that various fungi differ in their resistance to poisons, and that the limits of resistance even vary in the same species. The cathions Hg, H, and Cu, and the anions CN, CrO_4, Cr_2O_7 and OH are poisonous, while the halogen ions are not poisonous. In general, the results were found to be in accord with the dissociation theory.

The Physiological Action of Certain Plasmolyzing Agents. By RODNEY H. TRUE. *Botanical Gazette*, 26, 407–416.—The author has studied in the case of spirogyra the physiological action of the substances most used as plasmolyzing agents, cane-sugar, glycerine, sodium chloride and potassium nitrate. He is

of the opinion that all sodium and potassium salts injure spirogyra through their chemical and not their osmotic properties.

The Proteids of Cream. By E. F. Ladd. *J. Am. Chem. Soc.*, 20, 858–860.—The proteids of cream were divided into four groups, casein, albumen, albumoses, and peptones; the first group being precipitated by saturated alum solution, the second by boiling, the third by zinc sulphate, and the fourth by 80 per cent. alcohol. The analyses made show that no marked change took place in the proteids during the ripening of the cream.

Composition of Ohio Wines. By Albert W. Smith and Norman Parks. *J. Am. Chem. Soc.*, 20, 878–882.—The authors have analyzed twelve samples of wine of known purity and a number purchased in the open market. They find that in general their results do not differ much from published analyses of pure European wines from similar grapes, except in the percentages of glycerol and of ash, which are noticeably lower.

The Normal Chlorine of the Water Supplies of Jamaica. By Ellen H. Richards and Arthur T. Hopkins. *Tech. Quart.*, 11, 227–240.—From the results of analysis of seventy-six samples the authors have drawn a chart of the normal chlorine for the island of Jamaica giving the isochlors for 2.0, 1.0, 0.9, 0.8, 0.5 and 0.3 parts per hundred thousand. It has been found in general that the isochlors follow the coast line, being modified, however, by the excessive precipitation and evaporation which causes varying "dilution and concentration of chlorine." The fact that the interior of the island is but sparsely inhabited has made it possible to prepare a chart which is probably fairly accurate even though so few samples were analyzed.

Concentrated Feed Stuffs. By Joseph B. Lindsey. *Hatch Expt. Sta. Mass. Agr. Coll., Bull.* 56, 1–24. **Feeds Rich in Protein.** By Edward B. Voorhees. *N. J. Agr. Expt. Sta., Bull.* 131, 1–14.—These two bulletins contain the results of determinations of water, protein, and fat in various commercial feeding materials, such as cottonseed meal, gluten meal, wheat middlings, etc.

Commercial Fertilizers. *N. Y. Agr. Expt. Sta. Bull.* 145, 49–149; *Me. Agr. Expt. Sta. Bull.* 45, 1–24; *N. J. Agr. Expt. Sta. Bull.* 132, 1–61.

Baking Powders. *N. C. Agr. Expt. Sta. Bull.* 155, 51–56.

The Oil of Corn. By C. G. Hopkins. *J. Am. Chem. Soc.*, 20, 948–961.—As the result of a quite thorough examination of corn oil obtained from various sources the author considers its

percentage composition to be as follows: cholesterol, 1.37; lecithin, 1.49; stearin(?), 3.66; olein, 44.85; linolin, 48.19; total, 99.56.

Crystals of Sodium Chloride in Fluid Extract of Yerba Reuma and a Proximate Analysis of this Plant. By Lyman F. Kebler. *Am. J. Pharm.*, 71, 23–25.—The discovery of cubical crystals resembling salt in a fluid extract of Yerba Reuma about fifteen years old led the author to make a proximate analysis of the plant, following Dragendorff's scheme in the main. The most striking result obtained was the high percentage of ash and chlorides, amounting in one case to 34.12 per cent. of ash and 17.42 per cent. of chlorides calculated to sodium chloride.

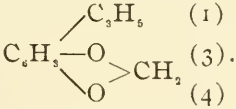
A Report of Progress of Investigations in the Chemistry of Wheat. By G. L. Teller. *Ark. Agr. Expt. Sta. Bull.* 53, 53–80.—In the course of this investigation analyses have been made of wheat gathered on each of forty-two consecutive days from the time of the setting up of the grain. The author finds a marked change in the relative proportion of the nitrogenous constituents at different periods of growth. The gliadin was found to increase largely from the earliest cutting until ripening, while the glutenin and amides decreased. The proportion of ash, amides, fats, fiber, dextrins and pentosans in the dry matter of the grain gradually decreased from the earliest stages. A more or less rapid decrease was also noted in the proportion of sucrose and of reducing sugar, while the proportion of starch rapidly increased up to a week before ripening. The proportion of total proteids in the dry matter steadily decreased up to a week before ripening and then gradually increased. The nitrogen compounds in the ripe grain were present in about the following proportions: amides, 1; edestin and leucosin, 3.5; glutenin, 10; gliadin, 16. The author also brings forward experimental evidence that the proteid designated "Proteose" by Osborne and Voorhees (*Am. Chem. J.*, 15, 468) is gliadin.

The Chemical Composition of the Carcasses of Pigs. By H. W. Wiley and Others. *U. S. Dept. Agr., Div. of Chem., Bull.* 53, 1–80.—This bulletin contains the results of analyses of the carcasses of eight breeds of American pigs, which had been cut up according to the prevailing method for the American market. In the samples, which were prepared with great care, the following determinations were made: Water, fat, ash, total nitrogen, nitrogen insoluble in hot water, nitrogen soluble in hot water but precipitated by bromine, and lecithin. The analytical results are given in a set of fifty-six tables, which are followed by a discussion. The bulletin also contains an abstract of the

literature relating to the separation of flesh bases from other nitrogenous bodies.

An Active Principle in Millet Hay. By E. F. Ladd. *Am. Chem. J.*, 20, 861–866.—The purpose of this work was to determine whether millet hay contained an extractive principle capable of producing the physiological disturbances that have followed the feeding of it to horses. The ground millet was extracted with petroleum ether and with ordinary ether without obtaining any unusual active principle. Tests made on the aqueous solution of the alcoholic extract, however, indicated the presence of some alkaloid or glucoside. From this aqueous solution, acidified with sulphuric acid, benzine extracted a light-yellow oily liquid, which, in some of its properties, resembled the glucoside *daphnin*, $C_{21}H_{34}O_{19}$, but differed from it in some respects. The physiological effect of this substance upon animals was found to be similar to that of the millet, but more marked.

The Chemistry of Sassafras. By Clemens Kleber. *Am. J. Pharm.*, 71, 27–32.—The chemistry of sassafras consists principally of the chemistry of its essential oils. The principal ingredient of the oil obtained from the bark of the root, which is what is ordinarily known as oil of sassafras, is safrol. This is the methylene ether of an allylpyrocatechin :



When oxidized this yields piperonal, and by further oxidation piperonylic acid. When safrol is boiled with alcoholic potash its allyl group is transformed into the isomeric propenyl group ($CH_3.CH : CH.$) thus forming isosafrol. The other constituents, present in much smaller quantity, are pinene, phellandrene, camphor, eugenol and cadinene (?). The oil of sassafras-leaves contains also considerable amounts of citral and geraniol as well as linalool, these last two alcohols being present also in the form of their acetic and valerianic esters. In the highest boiling, part is also a paraffin-like substance melting at 58° C.

Analysis of the Root of Hydrangea Paniculata, Variety Grandiflora. By August G. Luebert. *Am. J. Pharm.*, 70, 550–552.—The author has made a proximate analysis of the root of this plant, following Dragendorff's method of analysis. From the alcoholic and ethereal extracts was obtained a crystalline body melting at 178° C. The reactions of this substance indicate that it is not the *hydrangin* found in the closely allied species, *Hydrangea arborescens*, and the author proposes for it

the name *parahydrangin*. The amounts of other constituents contained in the root are also given.

Note on the Inversion of Cane Sugar in Official Syrups. By Louis Kahlenberg. *Pharm. Rev.*, 17, 10–12.—A critical review of an article on this subject by F. W. Haussman (*Am. J. Pharm.*, 70, 585).

Notes on Two Oils Containing Pulegone. Reported by Edward Kremers. *Pharm. Rev.*, 16, 412-417. **I. Mentha Canadensis L.** By Florence M. Gage.—The oil obtained by distillation of the fresh herb was examined. Its sp. gr. at 20° was 0.935, and it rotated the plane of polarized light 16°11′ to the right. The characteristic odor for carvacrol was obtained by Flückiger's reaction. By adding amyl nitrite and a trace of hydrochloric acid to the petroleum ether solution of the oil, crystals of nitrosopulegone melting at 79° were obtained. Crystals of pulegone oxime were also obtained corresponding to those from pennyroyal oil. **II. Pycnanthemum Lanceolatum Pursh.** By F. W. Alden.—The author has distilled both green and dry samples of the herb and in each case obtained a test for carvacrol. Using petroleum ether as a solvent, crystalline pulegone oxime was obtained without difficulty according to the method of Beckmann and Pleissner by the action of hydroxylamine hydrochloride and sodium bicarbonate on the oil. The crystals melted at 151°, and after solidification and cooling, the oxime melted at 117°–118°.

G. W. Rolfe, Reviewer.

Glycollic Acid: One of the Acids of Sugar Cane. By Edmund C. Shorey. *J. Am. Chem. Soc.*, 21, 45–50.—The author has obtained glycollic acid from Hawaiian cane-juice in quantities amounting to from seventy-five to eighty per cent. of the total acidity of the juice. He carefully differentiates this acid from malic and aconitic acids, and shows that his results are characteristic of glycollic acid alone. The possible bearing on sugar manufacture of the presence of this acid is also considered. The author believes it may be responsible for much of the caramel formed in molasses products as well as for the foaming of molasses massecuites in cars. The relation of the subject to the chemistry of the life processes of the growing cane is most interesting.

Light a Factor in Sugar Production. By H. A. Weber. *J. Am. Chem. Soc.*, 21, 53–59.—Much evidence, taken from the history of beet and sorghum culture in this country, has been collected by the author to demonstrate that the sugar content of the plant is dependent on the amount of direct sunlight received; hence, this should be an important consideration in deciding upon the most favorable climatic conditions for beet culture.

[Contribution from the Massachusetts Institute of Technology.]

REVIEW OF AMERICAN CHEMICAL RESEARCH.

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Arthur A. Noyes, Editor; Henry P. Talbot, Associate Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

INORGANIC CHEMISTRY.

Henry Fay, Reviewer.

Presidential Address. By Wolcott Gibbs. *Proc. Am. Assoc. Advancement Sci.*, 1898, 1–16. *Science*, 8, 233–243.—The author attempts to work out the theoretical relations existing between the complex derivatives of molybdic and tungstic acids with the acids of silicon and phosphorus.

On Some Relations among the Hydrates of the Metallic Nitrates. By J. H. Kastle. *Am. Chem. J.*, 20, 814–819.—The author has found that practically all of the salts of nitric acid may be referred to one of the hypothetical nitric acids, and that the nitrates can be grouped under five general classes. The first class, which includes all of the anhydrous nitrates, is regarded as an addition-product of the anhydride of nitric acid and the metallic oxide, $M^{I}_{2}O+N_2O_5 = 2M^{I}NO_3$. The second class includes a few nitrates, $HgNO_3.H_2O$ and $Th(NO_3)_4.4H_2O$, which are formed by the addition of ordinary nitric acid to a metallic base $M(OH)+HNO_3=MNO_3.H_2O$. To the third class belong a large number of nitrates of the bivalent and trivalent metals which are addition products of ortho-nitric acid and the metallic base derived as follows: $M^{II}(OH)_2+2H_3NO_4=M^{III}(NO_3)_2.4H_2O$; $M^{III}(OH)_3+3H_3NO_4=M^{III}(NO_3)_2.6H_2O$. Examples of this class are $Ca(NO_3)_2.4H_2O$, $Fe(NO_3)_3.6H_2O$, and a large number of double nitrates of which $2Ce(NO_3)_3.3Co(NO_3)_2.24H_2O$ is a type. The fourth class is formed by the addition of a base to the acid H_5NO_5, as $M^{II}(OH)_2+2H_5NO_5=M^{II}(NO_3)_2.6H_2O$, $M^{III}(OH)_3+3H_5NO_5=M^{III}(NO_3)_3.9H_2O$, and $M^{IV}(OH)_{IV}+4H_5NO_5=M^{IV}(NO_3)_4.12H_2O$. By the addition of pyronitric acid to a metallic

base the fifth class is formed : $M(OH)_2 + H_4N_2O_7 = M^{II}(NO_2)_2 . 3H_2O$ of which $Cu(NO_3)_2.3H_2O$ is an example. Including a number of cases of doubtful composition, 75 per cent. of all the normal nitrates described fall under one of these five classes. Most of the basic nitrates may also be classed under these headings as salts of some of the hypothetical nitric acids.

Liquid Ammonia as a Solvent. By E. C. Franklin and C. A. Kraus. *Am. Chem. J.*, 20, 820–836.—The authors have extended the work of Gore, Weyl, and Seeley on the solubility of various inorganic and organic substances in ammonia. Liquid ammonia was drawn off into a vacuum-jacketed tube and the substance to be tested was introduced into this tube in small quantity at a time and in case the substance was a solid, in the form of fine powder. Where there was any doubt about the solubility a measurement of the electrical conductivity was made. Tables are given which show the solubility of 157 inorganic salts and 250 organic substances.

Metathetic Reactions between Certain Salts in Solution in Liquid Ammonia. By E. C. Franklin and C. A. Kraus. *Am. Chem. J.*, 21, 1–8.—On account of the close relationship between liquid ammonia and water in solvent power, and in the power of dissociating many salts, it was supposed that metathetic reactions would take place in liquid ammonia as in water. This has been shown to be true. Sixteen nitrates were used to furnish the metallic ions ; and the sulphide, chloride, bromide, iodide, chromate, and borate of ammonia were used as precipitants. The tests were made by bringing the nitrates and the precipitants together in small vacuum-jacketed tubes and observing whether or not a precipitate was formed. Using ammonium chloride as precipitant no precipitates were produced in solutions of sodium and mercuric nitrates ; and from solutions of lithium, potassium, lead, silver, and copper, precipitates were produced only in concentrated solutions ; other nitrates gave precipitates at once. With ammonium bromide the results were the same except that here in addition potassium gave no precipitate and the other precipitations took place more slowly. Ammonium iodide produced precipitations only in solutions of strontium and barium salts. All the metals tested, with the exception of the alkalies, precipitated with ammonium sulphide. Judging from the color only a few of these substances were identical with the sulphides produced in water solution. The magnesium precipitate was found to be a double salt, $2MgS.(NH_4)_2S.xNH_3$, which evolved ammonia and hydrogen sulphide in the air. Ammonium chromate produces precipitates with all metals tested except lithium and sodium ; ammonium borate acts similarly with the exception that the potassium salt is soluble.

On the Solubility of Argentic Bromide and Chloride in Solutions of Sodic Thiosulphate. By Theodore William Richards and Henry Burnell Faber. *Am. Chem. J.*, 21, 167–172.—The authors have examined the solubility of silver bromide and chloride in sodium thiosulphate by agitating an excess of the pure silver salts with solutions of varying strength of the thiosulphate. After thorough agitation 5 cc. portions were drawn off and analyzed for silver. With increasing strength of the thiosulphate solutions the quantity of silver salt going into solution increased more rapidly than the increase in the quantity of thiosulphate used. The molecular ratio of the sodium thiosulphate to the dissolved salts at 35° C. for 200 grams of the crystallized salt to the liter of water was 1 : 0.78 for silver chloride and 1 : 0.52 for silver bromide. Evidence for the existence of a complex ion in such solutions was obtained by observing the change in the freezing-point ; it was found that by the addition of silver bromide the freezing-point was *raised* indicating the formation of a complex salt.

A New Gas. By Charles F. Brush. *J. Am. Chem. Soc.*, 20, 899–912.—During an investigation of the heat conductivity of various gases at extremely low pressures, it was found that gases were evolved from the glass on heating, which were only partly reabsorbed on cooling. Supposing the gas to come from the surface, some powdered glass was placed in the tube, and from this the gas seemed to be more freely evolved. On exposure to the air more of the gas was absorbed by the glass. On slight diminution of pressure the gas begins to come off, and the amount rapidly increases with the diminishing pressure. It is readily absorbed by soda-lime and phosphorus pentoxide. The heat conductivity at a pressure of 0.96 millionths of an atmosphere was found to be twenty times as great as that of hydrogen, and that of the pure gas would be 100 times that of hydrogen. If the inference is correct that the heat conductivity and the molecular velocity of gases are directly related, then the molecular velocity of the new gas is also one hundred times that of hydrogen. From this value of the molecular velocity, the density was found to be 0.0001, and the molecular weight, 0.0002. The author suggests that at anything like this molecular velocity, it would be quite impossible for a gas to remain in the atmosphere *unless the space above also contained it*, and therefore that the gas must fill all celestial space. On this assumption he has named the gas "etherion," and suggests that it may have some of the properties of the ether of the physicist.—Various investigators, notably Crookes, have recently claimed that all the phenomena described by Brush can be explained by the presence of a small quantity of water vapor in his apparatus.

Commercial Iron Silicides with a High Percentage of Silicon: Their Properties, Manufacture, and Uses. By G. de Chalmot. *J. Am. Chem. Soc.*, 21, 59–66.—The author has produced in the electric furnace iron silicides containing from twenty-five to fifty per cent. of silicon and probably consisting of the two compounds $FeSi_2$ and Fe_3Si_2. These silicides are crystalline, white or gray, hard and brittle, unalterable in the air, and can be cast well with sharp outlines and corners. These alloys are recommended for castings, on account of the smooth finish and high luster they are capable of taking; for anodes for electrolysis in aqueous baths; and for abrasives. Their manufacture is carried out by heating iron ore, river sand, and coke, in a special form of electric furnace.

The Preparation of Zirconium Nitrides. By J. Merritt Matthews. *J. Am. Chem. Soc.*, 20, 843–846.—The compound $ZrCl_4.8NH_3$ heated in a current of nitrogen decomposes and leaves as a gray residue the nitride Zr_3N_8. By heating zirconium tetrachloride in ammonia gas there is decomposition with the formation of the nitride Zr_2N_3.

Method of Preparing a Strictly Neutral Ammonium Citrate Solution. By A. D. Cook. *J. Am. Chem. Soc.*, 20, 585–586.—The author recommends stirring the citric acid solution after adding ammonia, the heat of neutralization being sufficient to drive off the excess of ammonia.

On the Segregation of Carbon in a Piece of Boiler Plate. By Henry Fay and Henry P. Talbot. *J. Am. Chem. Soc.*, 20, 614–617.—The authors have examined a piece of boiler-plate steel which, after having been twice annealed, cracked on flanging. On polishing and etching the surface, it was found that the steel was highly crystalline, and that the crystalline layer extended only part way into the plate on either side. Microscopical examination showed the carbon to be much segregated, and analysis of the borings taken from different parts of the plate varied from 0.03 to 0.156 per cent. of carbon. The probable cause of the brittleness was due to the annealing which was done at a temperature, 600°–750° C., at which granulation of mild steel takes place, as has been shown by the experiments of Stead.

ORGANIC CHEMISTRY.

J. F. Norris, Reviewer.

On Some Double Halides of Mercury. By J. N. Swan. *Am. Chem. J.*, 20, 613–633.—The double chlorides of mercury with aniline and the toluidines were prepared and studied. Aniline, *o*-toluidine, and *p*-toluidine gave salts of the composition, $2HgCl_2.BHCl$, $HgCl_2.BHCl$, and $HgCl_2.2BHCl$ where B repre-

sents the base. With *p*-toluidine but one salt was obtained which had the formula $HgCl_2.BHCl$. A mixed double halide of *o*-toluidine, $HgBr_2.BHCl$ and the following inorganic salts were also prepared : $3HgCl_2.MgCl_2.6H_2O$, $3HgCl_2.SrCl_2.XH_2O$, $3HgCl_2.BaCl_2.8H_2O$.

The Double Halides of Tin with Aniline and the Toluidines. By Robert L. Slagle. *Am. Chem. J.*, 20, 633–646.—A systematic search for the possible double chlorides of tin with aniline and the toluidines led to the preparation of the following salts which are fully described : With aniline, $SnCl_2.BHCl.H_2O$, $SnCl_2.2BHCl$, $SnCl_4.2BHCl$, and $SnCl_4.2BHCl.3H_2O$; with *o*-toluidine, $SnCl_2.BHCl.\frac{1}{2}H_2O$, $SnCl_4.3BHCl.2H_2O$; with *m*-toluidine, $SnCl_2.BHCl.\frac{1}{2}H_2O$, $SnCl_4.2BHCl.H_2O$; and with *p*-toluidine $SnCl_2.BHCl.\frac{1}{2}H_2O$, $SnCl_2.2BHCl$, $SnCl_4.2BHCl.H_2O$.

On Double Halides of Zinc with Aniline and the Toluidines. By Daniel Base. *Am. Chem. J.*, 20, 646–664.—The author gives a complete list of all the double halides of zinc with organic and inorganic bases which have been described. A study of the double chlorides of zinc and ammonium showed that but two salts are possible although eight have been described. These salts have the composition $ZnCl_2.2NH_4Cl$ and $ZnCl_2.3NH_4Cl$. A careful study of the possible double chlorides and bromides of zinc with aniline and the toluidines resulted in the formation of the following salts : With aniline, $ZnCl_2.2BHCl.H_2O$, $ZnCl_2.3BHCl.2H_2O$, $ZnBr_2.2BHBr.H_2O$; with *o*-toluidine, $ZnCl_2.2BHCl.2H_2O$, $ZnBr_2.2BHBr.H_2O$; with *m*-toluidine, $ZnCl_2.2BHCl$, $ZnCl_2.3BHCl$, $ZnBr_2.2BHBr.2H_2O$, $ZnBr_2.3BHBr$; and with *p*-toluidine, $ZnCl_2.2BHCl$, $ZnCl_2.3BHCl$, $ZnBr_2.2BHBr.H_2O$.

Sulphonation of the Paraffins. By R. A. Worstall. *Am. Chem. J.*, 20, 664–675.—The normal paraffins hexane, heptane, and octane are readily sulphonated when they are heated with fuming sulphuric acid in an open flask with a return-condenser. A yield of 30 to 40 per cent. of the monosulphonic acid was obtained when successive portions of the acid were used and the temperature was kept at the boiling point of the hydrocarbon. When the vapors of sulphur trioxide are passed through the boiling hydrocarbons disulphonic acids are produced. The yield of the latter was about 40 per cent. of the theoretical. The mono- and disulphonic acids are thick sirups which form barium and lead salts, which are very soluble in water and deliquesce rapidly.

The Formation of Hydrazides by the Action of Phenylhydrazine upon Organic Acids in the Cold. By Virgil L. Leighton.

Am. Chem. J., 20, 676–679.—Acetylphenylhydrazide was formed when a solution of phenylhydrazine acetate in acetic acid was allowed to stand four days. The formation of hydrazides from the phenylhydrazine salts of acids dissolved in the smallest quantity of the respective acid was shown to be a general reaction by the preparation of the hydrazides of formic, acetic, propionic, isobutyric, isohexylic, and heptylic acids.

Aliphatic Sulphonic Acids: II. Ethylenesulphonic Acids. By Elmer P. Kohler. *Am. Chem. J.*, 20, 680–695.—Ethylenesulphonic acid was prepared by decomposing 1,2-ethanedisulphone chloride with boiling water, by distilling 1,2-bromethanesulphone chloride under an increased pressure, and by heating the potassium salt of the acetic ester of isethionic acid at 185°. The acid forms well-crystallized ammonium, potassium, sodium, barium, and lead salts. The chloride of the acid prepared by treating the potassium salt suspended in chloroform with phosphorus pentachloride can be distilled under diminished pressure. Ethylenesulphonic acid is oxidized readily, the products being carbon dioxide, sulphuric acid, and water. Reduction is effected with difficulty: sodium amalgam in alkaline solution and zinc in acid solution are without effect. When the acid is heated with phosphorus and iodine, ethanesulphonic acid is formed. Ethylenesulphonic acid combines readily with water, especially in the presence of alkali, forming isethionic acid. When heated at 130° with hydrochloric and hydrobromic acids, addition-products are formed in which the halogen atoms are in the 2-position. With bromine, 1,1-bromethylenesulphonic acid is produced, the substitution being rapid and complete even at 0°.

The Ethers of Toluquinoneoxime and their Bearing on the Space Isomerism of Nitrogen. By John L. Bridge and Wm. Conger Morgan. *Am. Chem. J.*, 20, 761-776.—Toluquinone-*o*-oxime obtained by the action of nitrous acid on *m*-cresol forms well-characterized acetyl, benzoyl, and methyl ethers. The benzoyl ether of toluquinone-*m*-oxime, prepared in the same way from *o*-cresol, was shown to consist of a mixture of two isomeric substances, which were separated by fractional crystallization. The same ethers were obtained from the oxime formed by the action of hydroxylamine on toluquinone, and as no toluquinone-*o*-oxime was formed under these circumstances it seems highly probable that the isomerism is due to the space relation of the oxime group. Isomeric acetyl and methyl derivatives of toluquinone-*m*-oxime were also obtained. The compounds mentioned and a number of their bromine derivatives are described fully.

Camphoric Acid. By William A. Noyes. *Am. Chem. J.*, 20, 789–814.—By an error in his thermometer the author working with E. B. Harris, was led to think that the oxime of a ketone prepared from cis-campholytic acid (Harris, *this Rev.*, 3, 12), and the oxime of dimethyl-(1,3)-cyclohexanone (2) made by Kipping (*J. Chem. Soc.*, 67, 357) were identical. If the oximes were the same cis-campholytic acid would have the structure of Δ^1-tetrahydroxylic acid, $C_6H_7(CH_3)_2(1,3)COOH(2)$ and accordingly the synthesis of the latter acid was attempted. Although the preparation of the xylic acid will probably throw no light on the structure of cis-campholytic acid, the synthesis, which has been carried as far as the preparation of the neighboring xylic acid, is described, as a large number of new compounds has been prepared. The nitrile of the acid was obtained by the diazo reaction from 2-amino-*m*-xylene, but its saponification could not be effected. The xylidine required was obtained from commercial xylidine, in which it is present to the extent of about 2 per cent. An attempt was next made to prepare the xylic acid from dimethylcyclohexanone. In the preparation of the necessary dimethylpimelic acid, the dimethylpentanetetracarboxylic acid obtained as an intermediate product was isolated and found to have properties different from those which had been assigned to it. Dimethylcyclohexanone was prepared from dimethylpimelic acid, but the attempts to convert it into the hexahydroxylic acid through the cyanhydrin or cyanide were unsuccessful. The next method of preparation studied was the conversion of ethylidenediacetacetic ester into a cyclic compound by distillation under diminished pressure with chloroform and subsequent treatment with bromine (Knoevenagel, *Ann. Chem.* (Liebig), 281, 121). As only dimethyl-(1,3)-phenol-5-methylic-(2) acid, and its ethyl ester were obtained the method was abandoned. Unsuccessful attempts to prepare the xylic from acetobromxylene and acetoiodoxylene led to the preparation of 4-chlor-2-brom-*m*-xylene, 4-aceto-5-brom-1,3-xylene, bromxylic acid, $C_6H_2(CH_3)_2(1,3)COOH(4)Br(5)$, acetoiodoxylene, $C_6H_2(CH_3)_2(1,3)COCH_3(4)I(5)$, iodoxylylglyoxalic acid, $C_6H_2(CH_3)_2$, $CO.COOH$, iodomethylterephthalic acid, $C_6H_2CH_3(1)(COOH)_2(2,3)I(5)$ and two iodoxylic acids. The preparation of the neighboring xylic acid was finally effected from acetomesitylene. Improved directions for the preparation of mesitylene from acetone are given by which the yield is greatly increased. The mesitylene was converted into the acetyl derivative which, when oxidized, gave a mixture of about equal parts of 2,6-dimethyl terephthalic acid and dimethylphthalic acid. The acid ester of the former acid was converted into the amide, which was changed into an amine by means of sodium hypobromite. The amido group was replaced by iodine, which in turn was removed

by zinc dust and ammonia. The resulting acid was the neighboring xylic acid sought. The author proposes to reduce this acid.

On the Non-existence of Four Methenylphenylparatolyl Amidines. By H. L. Wheeler and T. B. Johnson. *Am. Chem. J.*, 20, 853–861.—The authors have carefully studied the four methenylphenylparatolyl amidines prepared according to Zwingenberger and Walther (*J. prakt. Chem.*, 57, 209), and have found that the substances are not pure compounds. By fractional crystallization the amidines were shown to consist of two or more substances. By crystallizing together mixtures of the constituents found, crystals were obtained which had the properties of the amidines described and which formed double platinum salts and picrates agreeing closely in melting-points with those given by Zwingenberger and Walther. The fact that but one methenylphenylparatolyl amidine exists destroys the conclusions of Walther (*J. prakt. Chem.*, 55, 43; 57, 229) as to the structure of the anilides. Methenylmethylphenylamide-phenylimidine, $C_6H_5(CH_3)N{-}CH{=}NC_6H_5$, was prepared by mixing methylaniline with methylisoformanilide, by adding a mixture of methylaniline and formanilide to an excess of phosphorus trichloride, and by heating methenyldiphenylamidine with an excess of methyl iodide. The compound is a colorless oil, which forms a hydrochloride and a double chloride with gold.

Creatin and Its Separation. By E. F. Ladd and P. B. Bottenfield. *Am. Chem. J.*, 20, 869–870.—The amount of creatin in ox flesh was determined by the methods of Neubauer, Stradler, and Liebig and was found to be 0.250, 0.234, and 0.215 respectively. The same methods of analysis applied to the flesh of a dog gave 0.242, 0.230, and 0.218 per cent. The authors consider the high results obtained by Neubauer's method the most accurate.

A Double Citrate of Zirconium and Ammonium. By S. H. Harris. *Am. Chem. J.*, 20, 871–872.—By adding an aqueous solution of ammonium citrate to a solution of zirconium chloride a double salt of the composition $Zr_2(C_6H_5O_7)(NH_4)_3$ was formed as a curdy white precipitate which was very deliquescent when dried.

On the Constitution of the Phenylhydrazones. By Paul C. Freer. *Am. Chem. J.*, 21, 14–64.—Two possible constitutions can be assigned to the compounds of phenylhydrazine with ketones and aldehydes:

$$(1)\quad \begin{matrix} R'RHC \\ | \\ R''_3C.C:N.NHC_6H_5 \end{matrix} \qquad \text{and} \qquad (2)\quad \begin{matrix} RR'C \\ \| \\ R''_3C.C.NH.NHC_6H_5. \end{matrix}$$

When phenylhydrazine reacts with an aldehyde or a ketone there is, in all probability, a direct addition-product formed, which immediately loses water and passes into the hydrazone. This elimination of water could take place in two ways and would yield either a true hydrazone (formula 1) or a hydrazo compound (formula 2). That such addition-products are formed was shown by the fact that ethereal solutions of aldehyde and methylethyl ketone, when cooled to —20° and mixed with phenylhydrazine, gave precipitates which dissolved and changed into hydrazones. The phenylhydrazones can be divided into two classes: those which are readily oxidized in the air and change to non-crystallizable tars with the evolution of gas, such as the phenylhydrazones of acetone, other aliphatic ketones, and acetophenone; and those which are perfectly stable or do not yield oxidation-products, such as the derivatives of aceto-acetic ester, pyruvic acid, and benzophenone. It is concluded that the hydrazones of the first class are probably hydrazo compounds and have the structure represented by formula (2) while those of the second class are true hydrazones (formula 1). This conclusion is justified by the fact that acetone-*p*-bromphenylhydrazone, when carefully subjected to the action of the air, is quantitatively changed to a red explosive azo compound, which is reduced by sodium amalgam to the original hydrazone. The azo compound exhibited the characteristic properties of true azo bodies, forming a crystalline perbromide, which decomposed in the manner typical of such compounds. Since the formation of an azo compound from a true hydrazone by oxidation seems highly improbable, formula (2) must be assigned to acetone-*p*-bromphenylhydrazone. The phenylhydrazone of acetophenone formed derivatives analogous to those described above. The two classes of hydrazones show a marked difference in behavior with benzoyl chloride. Acetonephenylhydrazone, which is readily oxidized to an azo compound, and has the hydrazo structure, readily reacts with benzoyl chloride and forms a product containing two benzoyl radicles, whereas benzophenone, having the hydrazone structure, reacts with difficulty and the resulting compound contains but one benzoyl group. This method of deciding structure can not be applied to the large number of hydrazones which do not react with benzoyl chloride. If the phenylhydrazones are formed by the elimination of water from an addition-product of the ketone and phenylhydrazine, it is possible that one ketone might yield two isomeric derivatives represented by the above formulas. Smith and Ransom (*Am. Chem. J.*, 16, 108), have proved the existence of two benzoïnphenylhydrazones and considered them to be geometrical isomers. The author's method of study shows that the two substances have different structures. One is readily

oxidized to an azo compound by nitrogen trioxide with which it forms a red crystalline addition-product, which in turn forms a characteristic perbromide. The other, when treated in the same way, gives a white tetrazone. *β*-Benzoïnphenylhydrazone is converted into an isomeric substance by benzoyl chloride. The two acetaldehydrazones were studied in the same way but the results were not conclusive, since the two compounds change from one form to the other with great readiness. Doubt is thrown upon the structure of the compound prepared by oxidizing acetoaceticesterphenylhydrazone with mercuric oxide. The facts that the compound does not give a perbromide, that it is not reduced to the original hydrazone by sodium amalgam, and that it can be heated above its melting-point without decomposition, show that it is not benzene-azo-*β*-oxycrotonic ester. Chloraldehyde hydrate and phenylhydrazine yielded a substance of the structure

$$C_6H_5.NH.NH.CH_2.CH : N.NH.C_6H_5.$$

Note on the Action of Liquid Hydriodic Acid on Ethyl Ether. By F. G. Cottrell and Roy Ravone Rogers. *Am. Chem. J.*, 21, 64–67.—When ether and liquid hydriodic acid were mixed a vigorous reaction took place and water and ethyl iodide were formed. By conducting the experiment in a specially designed piece of apparatus, an almost quantitative yield of ethyl iodide was obtained. This is noteworthy since Silva has shown (*Compt. rend.*, 81, 323) that with gaseous hydriodic acid alcohol was also formed.

Certain Alkaloidal Periodides and the Volumetric Estimation of Alkaloids as Higher Periodides. By A. B. Prescott and H. M. Gordin. *J. Am. Chem. Soc.*, 20, 706–728.—By pouring a solution of atropine in dilute hydrochloric acid into a large excess of Wagner's reagent a periodide is precipitated containing nine iodine atoms. Under similar conditions strychnine, brucine, and aconitine give periodides containing seven atoms of iodine, while with morphine the precipitate contains but four atoms of iodine. The authors show that the formation of these perhalides is quantitative, and describe the volumetric estimation of the above alkaloids based on this reaction. Two double iodides of atropine and mercury are also described.

On Tetraphenylmethane. By M. Gomberg. *J. Am. Chem. Soc.*, 20, 773–780.—Improved directions for the preparation of tetraphenylmethane from triphenylmethanehydrazobenzene are given. A molecular weight determination of the hydrocarbon and an analysis of the tetranitro-derivative furnish further evidence for the composition which has been assigned it. This is also shown by the fact that the nitro-derivative does not

form a sodium salt, whereas dinitrodiphenylmethane and trinitrotriphenylmethane give highly colored sodium compounds.

Hydrazo- and Azo-derivatives of Triphenylmethane. By M. Gomberg and A. Campbell. *J. Am. Chem. Soc.*, 20, 780–790.—Well-crystallized hydrazo-compounds were formed by treating triphenylbrommethane with a large number of hydrazines. They oxidize in the air and form salts with dry hydrochloric, oxalic, picric, and other acids. The hydrazo-compounds are readily oxidized by amyl nitrite to azo-derivatives, which give off their nitrogen quantitatively when heated.

A Periodide of Triphenylbrommethane. By M. Gomberg. *J. Am. Chem. Soc.*, 790–793.—Triphenylbrommethane unites with iodine in benzene solution and forms a periodide of the composition $(C_6H_5)_3CBr.I_4$, which crystallizes in hollow hexagonal crystals.

Perhalides of Quinoline. By P. F. Trowbridge. *J. Am. Chem. Soc.*, 21, 66–72.—A large number of perhalides of quinoline containing one, two, and four added halogen atoms are described. Halogen addition-products of the compounds formed by the union of quinoline and methyl chloride, bromide, and iodide were also prepared.

Analysis of Aqueous Alcohol. By Chester B. Curtis. *J. Phys. Chem.*, 2, 371–375.—The amount of alcohol in an aqueous solution can be estimated by determining the quantity of toluene necessary to cause a cloudiness in the solution. The method can be used only when the solution contains above eighty-five per cent. of alcohol and gives results as accurate as those obtained by the pycnometer test.

The Physical and Chemical Properties of Lithium Benzoate and Lithium Salicylate. By Lyman F. Kebler. *Am. J. Pharm.*, 71, 57–64.—The properties of samples of lithium salicylate and benzoate, which are on the market, and of the carefully purified salts, are described in detail.

The Electric Current in Organic Chemistry. By Edgar F. Smith. *Proc. Am. Assoc. Advancement Sci.*, *1898*, 179–194.—This paper is a historical address delivered by the author as chairman of the Chemical Section of the Association.

GEOLOGICAL AND MINERALOGICAL CHEMISTRY.

W. O. Crosby, Reviewer.

Notes on North Carolina Minerals. By J. H. Pratt. *J. Elisha Mitchell Sci. Soc.*, 14, *pt.* 2, 61–83. The notes on four of

the nine minerals considered in this article, wellsite, anorthite, cyanite and zircon, have peen published elsewhere and noticed in this Review. The remaining species are chabazite, anthophyllite, enstatite, enstatite (bronzite), and emerald beryl. The chabazite occurs as minute crystals coating feldspar, hornblende and corundum and intimately associated with the wellsite, in a corundum mine in Clay County. Two analyses are given; and the ratio of Al_2O_3 to the protoxide bases is found to be somewhat below the normal. The anthophyllite, which occurs in dunite rock near Bakersville, was originally described by Penfield in 1890, before the locality was known. A new analysis is given, and Penfield's analysis is quoted for comparison, the two agreeing very closely, and closely approximating the normal composition. The enstatite forms rock masses bordering the dunite of Corundum Hill. The analysis indicates the admixture of 35 per cent. of serpentine and 20.5 per cent. of talc, the pure enstatite forming but 44.5 per cent. of the whole. The bronzite forms with an emerald-green diopside a tough rock (websterite) in the dunite of the Tuckaseegee Valley; and the websterite also varies to a nearly pure bronzite rock. The analysis and physical characters show this to be a very typical bronzite. The emerald beryl occurs in a vein of pegmatite, and is in part of gem quality; but it has not been analyzed. All of the new analyses of the foregoing minerals were made by Chas. Baskerville of the N. C. Geological Survey.

The Origin and Chemical Composition of Petroleum. A Symposium. By S. P. Sadtler, S. F. Peckham, David T. Day, Francis C. Phillips and Charles F. Mabery. *Proc. Am. Phil. Soc.*, 36, 93–140.—This paper is a valuable summary of our knowledge of petroleum and natural gas, and in a measure of all of the native bitumens. Prof. Sadtler discusses the genesis and chemical relations of petroleum and natural gas; and rejecting all the theories of the inorganic origin of these bodies, and weighing carefully the rival theories of their derivation from animal tissues and from plants, concludes, partly from original experiments with linseed oil, that both the theories of their organic origin are required to explain all the facts. Prof. Peckham's contribution is on the nature and origin of petroleum, setting forth at some length the facts which appear to sustain the distillation theory, which is made to cover all the native bitumens from natural gas to asphaltum. Dr. Day develops a suggestion as to the origin of Pennsylvania petroleum which is a modification of Mac Gonigle's theory that the Pennsylvania oils have been derived by distillation from the underlying Silurian strata, the transfer from the lower to the higher formations, with a notable increase in density and loss of sulphur,

having, according to Day, been accomplished, not by distillation but by an upward filtration through beds of shale. Prof. Phillips discusses and accepts provisionally Mendeléeff's theory that metallic carbides have been produced deep in or below the earth's crust, and that these carbides have been decomposed by steam, giving rise to the various hydrocarbons of oil and gas; and in accordance with this view the author argues strongly against the view that petroleum occurring in the cavities of fossils is indigenous in them. Prof. Mabery, in considering the composition of American petroleum, notes the progress of our knowledge, the difficulty of correlating the composition or specific gravity with the distribution or geological occurrence. Even the high sulphur oils, which some have regarded as peculiar to limestones, are shown to be also very typically developed in sandstones and shales. The importance and feasibility of a general system of classification on the basis of the series of hydrocarbons which constitutes the main body of the crude oils are discussed at some length.

The Genesis of Bitumens, as Related to Chemical Geology. By S. F. Peckham. *Proc. Am. Phil. Soc.*, 37, 108–139.—This paper is a sequel to the preceding symposium; but the author contents himself with a very general discussion of the geology of the bitumens and especially of petroleum, and a restatement of the facts supporting the distillation theory of petroleum and natural gas.

M. L. Fuller, Reviewer.

On Dikes of Felsophyre and Basalt in Paleozoic Rocks in Central Appalachian Virginia. By N. H. Darton. **Notes on the Petrography.** By Arthur Keith. *Am. J. Sci.*, 156, 305–315.—A third locality of igneous rocks in the Central Appalachian region has recently been discovered by Mr. Darton. Both basic and acidic dikes are represented, the latter belonging to the granite family and most nearly resembling felsophyre. Petrographic descriptions of both types are given by Mr. Keith, supplemented by an analysis of the felsophyre by W. F. Hillebrand.

Causes of Variation in the Composition of Igneous Rocks. By T. L. Walker. *Am. J. Sci.*, 156, 410–415.—A brief review is given of the usual theories of magmatic differentiation. The author considers that none give satisfactory explanations of all the phenomena observed, especially of the excessively basic centers of certain eruptive masses. Attention is called to the fact that certain homogeneous solutions remaining for a long time at constant temperatures become gradually more concentrated in the lower portion, and it is urged by the author that a similar concentration probably occurs in complex silicate mag-

mas, especially when near the temperature of consolidation. The material along the borders solidifies before the differentiation is far advanced, representing the original composition. Differentiation and solidification progress simultaneously, and hence the central portions will have suffered the greatest changes. In the upper horizons of the eruptive there would be an increase in *acidity* towards the center; the middle horizons would show little differentiation, while the lower horizons would show an increase in *basicity* towards the center. These relations are illustrated graphically by a diagram. It is not considered that this is ever a sole cause of differentiation. The ability of gravitation to produce concentration in solutions is denied by some physicists, but is upheld by those who have investigated it most carefully.

On the Associated Minerals of Rhodolite. By W. E. Hidden and J. H. Pratt. *Am. J. Sci.*, 156, 463–468.—The more common associated minerals of this new variety of garnet are quartz, corundum, pleonaste, gahnite, chromite, iolite, staurolite, monazite, zircon, gold, and sperrylite. The occurrence of each is described and analyses by Chas. Baskerville are given for gahnite and iolite.

Platinum and Iridium in Meteoric Iron. By John M. Davison. *Am. J. Sci.*, 157, 4.—After treating the Coahuila and Toluca meteoric irons with hydrochloric acid, there remained in each case a fine black residue consisting of irregular or tetragonal crystals of rhabdite, carbon, and some stony matter. Analyses of these sediments showed the presence of both platinum and iridium. From 608.6 grams of Coahuila iron there were obtained 0.014 gram of platinum, and 0.0015 gram of a black powder, probably iridium. The amounts obtained from the Toluca iron were considerably less. Unsuccessful search was made for microscopic diamonds.

Mineralogical Notes: Analyses of Tysonite, Bastnäsite, Prosopite, Jeffersonite, Covellite, Etc. By W. F. Hillebrand. *Am. J. Sci.*, 157, 51–57.—The analyses of the following minerals were made in the laboratory of the U. S. Geological Survey. 1. Tysonite and bastnäsite. Analyses of fine specimens from Cheyenne Mt., near Pikes Peak, Col., agreed essentially with those of Allen and Comstock. The formulas $R'''F'_3$ for tysonite and $R'''(F',CO''_3)$ for bastnäsite, which in the absence of fluorine determinations have not hitherto been confirmed, are shown to be correct. The analyses show some 40 per cent. of Ce_2O_3 (including ThO_2), with a little less of the La group. 2. Prosopite. A beautiful pale green mineral from Utah, supposed by Kunz to be utahlite, proved on analysis to be prosopite, mixed

with quartz and fluorite (?), and colored by some copper salt. Comparison with Altenberg and Pikes Peak prosopites shows a close agreement except in amounts of F and H_2O, the variation of these two affording further evidence as to their mutual replacement by one another. 3. Jeffersonite. An analysis of a brown mineral from Franklin Furnace, N. J., agrees closely with that of jeffersonite but its physical properties differ from hitherto published data of that mineral. The author considers the analysis chiefly valuable as showing a wide range of composition for the mineral. 4. Analyses are also given for covellite, enargite, and a blue stalactite from Butte, Montana, and a fibrous sulphate corresponding to the empirical formula $(FeMn)_4(ZnMg)_2Al_2(SO_4)_9.65H_2O$ from near Whitehall, Montana.

On the Chemical Composition of Tourmaline. By S. L. Penfield and H. W. Foote. *Am. J. Sci.*, 157, 97–125.—This important mineralogical contribution consists essentially of an elaborate review and critical discussion of the investigations of Rammelsberg, Riggs, Jannasch and Kalb, and others upon the constitution of tourmaline. Two new and carefully executed analyses are given which agree closely with those of previous investigators. Rammelsberg's conclusion that all tourmalines are derived from the acid H_6SiO_5 was based on analyses which the authors have shown to be defective. On applying the necessary corrections, however, the general formula $H_{20}B_2Si_4O_{21}$ may be derived, which agrees with that obtained by Riggs, Jannasch, and Kalb, and the authors. A critical examination of the many published analyses, taken in connection with their own analyses of exceptionally pure specimens, leads the authors to the conclusion that all varieties of tourmaline are to be considered as salts of the acid $H_9Al_3(B.OH)_2Si_4O_{21}$, in which the complex aluminium-borosilicic acid radical exerts a *mass effect* by virtue of which the remaining hydrogens may be replaced by numerous metals of essentially different characters without any pronounced effect on crystalline form. The table of the ratios $R' : R'' : R''' : H$, derived from some 35 analyses, including practically all varieties thus far investigated, shows that although certain prominent types undoubtedly exist, the ratios do not approach closely enough to rational members to give definite formulas.

On the Occurrence of Cubanite at Butte, Montana. By Horace V. Winchell. *Am. Geol.*, 22, 245.—An analysis of a brass-yellow ore of copper gave results agreeing closely with both the theoretical composition and with previous analyses of cubanite.

The Origin of the Archean Igneous Rocks. By N. H. Winchell. *Am. Geol.*, **22**, 299–310. It has been previously assumed that the oldest known rocks were of the acid type, but the author has recently endeavored to show that the ferro-magnesian greenstones may be considered as the existing representatives of the original crust, and that the acid rocks are of a later period. T. Sterry Hunt had previously reached a similar conclusion as to the nature of the primitive crust on chemical grounds, and had explained the minerals of the acid rocks as derived by leaching from the ferro-magnesian types, giving as an example of the process, the occurrence of potash feldspar in geodes, etc., in the Keweenawan diabase. The author holds, on the contrary, that the feldspar is probably a true aqueous deposit of material derived from extraneous sources, and that a more probable view as to the origin of the acid rocks is that they have been derived from the fusion of deeply buried sediments. Several supposed examples of such derivation are described, and the process is suggested as a general explanation of the granites throughout Minnesota. The acid elements, however, and especially the potassium, could not have been derived from the basic greenstones. The conclusion is that for these elements we must look to the atmosphere as it existed upon the original congelation of the crust, and this leads up to the question of the chemical properties and volatility of potassium, and its probable activity under Archean conditions.

On the Dikes in the Vicinity of Portland, Maine. By E. C. E. Lord. *Am. Geol.*, **22**, 335–346.—Both basic and acid types are represented in the dikes of Casco Bay and vicinity, but only the basic varieties are considered in detail. Of these, olivine-diabase-porphyry is represented by 24 dikes, while enstatite-diabase-porphyry and camptonyte are represented by two each. With one exception they have a persistent strike of N. 55° E. Petrographical and mineralogical descriptions are given for each variety and its alteration discussed. Analyses are given for anorthoclase, barkevicitic hornblende, and the enstatite-diabase-porphyry. From the field relations and composition it is concluded that the Casco Bay dikes are genetically related to those of Kennebunkport and Bald Cliff. The similarity in composition to augite-syenite from Norway suggests the possibility that certain of the dikes at least are offshoots of an underlying parental rock of that description. Their age is less than that of the associated pegmatites, and it is conjectured that they are coincident with a period of volcanic activity towards the close of the Devonian, and contemporaneous with the granitic intrusions of Nova Scotia and New Brunswick.

[Contribution from the Massachusetts Institute of Technology.]

REVIEW OF AMERICAN CHEMICAL RESEARCH.

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Arthur A. Noyes, Editor; Henry P. Talbot, Associate Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

GEOLOGICAL AND MINERALOGICAL CHEMISTRY.

M. L. Fuller, Reviewer.

Thomsonite and Lintonite from the North Shore of Lake Superior. By N. H. Winchell. *Am. Geol.*, **22**, 347–349.—The paper describes the properties, associations, and localities of both minerals. An analysis of lintonite is given and the reasons (optical) for its separation from mesolite or thomsonite, to which it might be referred on chemical grounds.

Thalite and Bowlingite from the North Shore of Lake Superior. By N. H. Winchell. *Am. Geol.*, **23**, 41–44.—The treatment of the subject is mainly descriptive, but includes a new analysis of thalite.

Chlorastrolite and Zonochlorite from Isle Royale. By N. H. Winchell. *Am. Geol.*, **23**, 116–118.—The paper includes descriptions of both minerals, with an analysis of the former.

On the Occurrence of Quenstedtite near Montpelier, Iowa. By Otto Kuntze. *Am. Geol.*, **23**, 119–121.—The sandstone bed of a small creek is locally incrusted above the water with a dry yellow mineral which on analysis proved to be nearly pure quenstedtite ($Fe_2(SO_4)_3 + 10H_2O$), a mineral previously described by Dana as coming only from Chile. On exposure to direct sunlight it rapidly decomposes and disappears, but under favorable conditions may accumulate to a thickness of 1 or 2 inches during a single summer. The material is derived from the decomposition of fine scales of pyrite, with which the sandstone is filled.

Clay Resources of Missouri. By H. A. Wheeler. *Eng. Min. J.*, 66, 426–427.—The paper includes statistics relating to the character, use, output, and price of the clays, with a description of the condition of the industry. Analyses are given for white-ware clays, fire clays, potter's clays, shales, brick clays, and gumbo clays.

The Alkaline Reaction of Some Natural Silicates. By F. W. Clarke. *J. Am. Chem. Soc.*, 20, 739–742.—On adding distilled water containing a very little alcoholic phenolphthalein to samples of certain finely pulverized silicates, including micas, feldspars, zeolites, etc., alkaline reactions were immediately obtained. As would be expected, the colors were most intense in the case of those minerals which in nature are most subject to alteration. Similar results were also obtained from tests upon the common igneous rocks. The rapidity of the action is a striking feature.

Petroleum Inclusions in Quartz Crystals. By Chas. L. Reese. *J. Am. Chem. Soc.*, 20, 795–797.—Crystals of quartz with petroleum inclusions from Marshall Co., Ala., are described and illustrated. The petroleum was recognized by its fluorescence, odor, and combustibility.

Mineral Resources of Cuba. By Raimundo Cabrera, translated by L. E. Levy. *J. Franklin Inst.*, 146, 26–41.—Descriptions and analyses are given of the more important ores and economic deposits including asphaltum, phosphate rock, and the ores of gold, silver, lead, copper, iron, and manganese.

The Slate Regions of Pennsylvania. By Mansfield Merriman. *Stone*, 17, 77–90.—A description is given of each of the principal slate-producing regions, accompanied by tables of statistics relating to the output and properties of the slates. The probable resistance to corrosion by smoke, sulphurous vapors, etc., was tested by treatment for 63 hours in a 2 per cent. solution of $HCl + H_2SO_4$. The results are given in a tabulated form.

The Bayport, Michigan, Quarries. By A. C. Benedict. *Stone*, 17, 153–164.—The limestone from these quarries is used as road metal, building stone, or burned for lime. Analyses are given for the building stone and lime varieties.

GENERAL AND PHYSICAL CHEMISTRY.

A. A. Noyes, Reviewer.

A Revision of the Atomic Weight of Nickel. II. The Determination of Nickel in Nickelous Bromide. By Theodore

William Richards and Allerton Seward Cushman. *Proc. Am. Acad.* 34, 327–348.—The authors have found that the samples of nickel bromide previously used (see *this Rev.*, 4, 27) for determining the ratios $NiBr_2 : 2AgBr$ and $NiBr_2 : 2Ag$ contained about 0.1 per cent. of sodium bromide, this contamination having been introduced in the final sublimation of the samples in a porcelain tube. After a fruitless attempt to obtain a pure product by subliming in a platinum-lined tube, the authors decided to make a complete analysis of the slightly impure substance by determining the exact amount of sodium bromide and the amount of nickel present, in the same samples in which the bromine had peen previously estimated. With this end in view it was attempted to precipitate the nickel electrolytically, as had been done by Winkler, but experiments made by dissolving weighed portions of pure spongy nickel and electrolyzing in a platinum dish showed that the weight deposited was always appreciably greater than that of the nickel originally taken (0.2 per cent. greater when the method of Winkler of drying at 50° was followed), probably owing to the inclusion of mother-liquor and of hydrogen. The following method was therefore adopted: the weighed nickel bromide contained in a platinum boat was reduced with moist hydrogen at a comparatively low temperature, the hydrogen replaced by dry air, and the boat weighed; the residue was then digested repeatedly with pure water and the bromine in the filtrates was precipitated and weighed as silver bromide. The possible errors in this procedure were carefully investigated: thus it was shown by rinsing out the cooler parts of the combustion tube with nitric acid that no nickel bromide was lost by volatilization; by exposing the spongy nickel to the air that no oxidation took place; by burning it in air in a combustion tube that no water was produced, and, therefore, that no hydrogen was occluded; and by qualitative analysis of the water extract that it contained nothing but sodium bromide and some nickel dissolved by the action of water on the metal itself. Making proper corrections for the amount of sodium bromide present, the mean values of the atomic weights calculated from the different ratios determined are as follows: 58.703 from $NiBr_2 : 2AgBr$; 58.704 from $NiBr_2 : 2Ag$; and 58.709 from $NiBr_2$: Ni. As the final value based on all determinations, 58.706 is adopted. The article closes with a criticism of the work of previous investigators on the same subject.

A Revision of the Atomic Weight of Cobalt. II. The Determination of the Cobalt in Cobaltous Bromide. By Theodore William Richards and Gregory Paul Baxter. *Proc. Am. Acad.*, 34, 351–369.—This investigation is closely analogous to the one on nickel just reviewed. The cobalt bromide was

proved to contain about 0.1 per cent. of impurity by reducing it in hydrogen, leaching with water, evaporating, and weighing the residue, this being admissible in this case since the cobalt dissolved by the water is almost all precipitated in the cobaltic form during the evaporation by the oxidizing action of the air. The residue was found to consist mainly but not wholly of sodium bromide. The final values of the atomic weights derived from each of the ratios determined are: $CoBr_2 : 2AgBr$, 58.995; $CoBr_2 : 2Ag$, 58.987; $CoBr_2 : Co$, 58.998, the final average adopted being 58.995. At the close of the article various criticisms made by Winkler are answered.

Sixth Annual Report of the Committee on Atomic Weights. Results Published in 1898. By F. W. Clarke. *J. Am. Chem. Soc.*, 21, 200–214.—The following is a summary of the results published in 1898, the values given by the author in his last year's table being appended in parentheses.

Oxygen, Keiser	15.880	(15.879)
Nitrogen, Dean	14.055	(14.04)
Boron, Armitage	10.959 10.928	(10.95)
Zinc, Morse and Arbuckle	65.457	(65.41)
Cadmium, Morse and Arbuckle	112.377	(111.95)
Selenium, Lenher	79.314	(79.02)
Tellurium, Metzner	127.9	(127.49)
" Heberlein	126.98	(127.49)
Zirconium, Venable	90.78	(90.40)
Thorium, Brauner	232.42	(232.63)
Praseodymium, Jones	140.46	
" Von Schele	140.40	(143.6)
" Brauner	140.95	
Neodymium, Jones	143.6	
" Boudouard	143.045	(140.8)
" Brauner	143.5	

The methods used by Armitage in the case of boron have been subjected to much unfavorable criticism. At the close of the article the author gives his revised table of atomic weights by the side of those of Richards and the German Committee. It is much to be regretted that both the author and the German Committee have ignored the usual practice in regard to significant figures, curiously enough in opposite directions, the latter retaining such a number of figures that the last one is certain, while the author retains always two decimals without reference to the probable accuracy of the result.

The Nature of Valence. By F. P. Venable. *J. Am. Chem. Soc.*, 21, 192–200; 220–231.—Besides presenting at length the views of other chemists the author proposes the hypothesis that valence is not an inherent property of the single atom, but is the resultant of the mutual influence of the atoms entering into com-

bination, "the number of atoms forming one molecule being purely a matter of equilibrium and dependent on the motion of those atoms." The author does not show, however, that this indefinite hypothesis leads to any specific or tangible results. In regard to it the reviewer would remark, somewhat in line with Lothar Meyer's statement quoted by the author, that it is only in so far as valence can be regarded as a constant property of the atom, or in so far as the conditions of its variation can be specifically stated, that the concept of valence has any scientific value.

The Rise of the Theory of Electrolytic Dissociation, and a Few of Its Applications in Chemistry, Physics, and Biology. By HARRY C. JONES. *Johns Hopkins Hospital Bull.*, 87, 1–10. —A brief address on the subject read before the medical society.

Natural Science of the Ancients as Interpreted by Lucretius. By F. P. VENABLE. *J. Elisha Mitchell Sci. Soc.*, 15, 62–75.

The Solubility of Iodide in Dilute Potassium Iodide Solutions. By A. A. NOYES AND L. J. SEIDENSTICKER. *J. Am. Chem. Soc.*, 21, 217–220.—The authors show that the excess of iodine dissolved by potassium iodide solutions over that dissolved by pure water is proportional to the concentration of the iodide (between the concentrations 0.1 and 0.006 normal), and that this result is in accord with the assumption that the complex salt in solution has the formula KI_3, or more correctly that its anions which alone are present in important amounts have the corresponding formula I_3.

The Velocity of the Reaction between Silver Acetate and Sodium Formate. A Reaction of the Third Order. By ARTHUR A. NOYES AND GEORGE T. COTTLE. *J. Am. Chem. Soc.*, 21, 250–256.—The velocity of the reaction, measured at 100°, is shown to be proportional to the concentration of the formate and the square of that of the silver salt corresponding to the fact that one molecule of the former substance reacts with two of the latter.

H. M. GOODWIN, REVIEWER.

Absorption of Gases in High Vacuum. By C. C. HUTCHINS. *Am. J. Sci.*, 157, 61–63.—It was found that of the several gases investigated, namely cyanogen, nitrogen, iodine, and oxygen, the latter is by far the least rapidly absorbed by the discharge in a vacuum tube, and in consequence the vacuum in a tube containing this gas is less rapidly raised than in tubes filled with the other gases. The author suggests therefore introducing mercuric oxide around an auxiliary anode as an efficient and simple device for maintaining X-ray tubes at the exhaustion of maximum efficiency.

Note on the Transference Number of Hydrogen. By Wilder D. Bancroft. *J. Phys. Chem.*, 2, 496–497.—This note refers to Hopfgartner's paper in connection with the work of McIntosh on the transference number of hydrogen (see *this Rev.*, 5, 101). The discrepancies between the determinations by these investigators and those of Bein and Kohlrausch cannot yet be satisfactorily explained.

On the Heat of Solution of Liquid Hydriodic Acid. By F. C. Cottrell. *J. Phys. Chem.*, 2, 492–495.—The liquid acid contained in a sealed glass tube was broken in a calorimeter of 500 cc. capacity and the rise of temperature noted. The mean of three determinations gave 148.3 K (1K = 100 g. cal. at 12°). Corrected for that portion of the acid present as saturated vapor in the sealed tube the value is 147.8. From this the molecular heat of condensation of the gas is computed to be 42.8 K.

Variance of the Voltaic Cell. By Wilder D. Bancroft. *J. Phys. Chem.*, 2, 227, 240.—The author takes exception to Nernst's method of application of the phase rule to the Voltaic cell, and then illustrates its use in the case of numerous cells; the application of Le Chateliers theorem in predicting qualitatively the changes in the electromotive force produced by changes in the variables on which the electromotive force depends, is also illustrated by examples.

Electromotive Force between Amalgams. By Hamilton P. Cady. *J. Phys. Chem.*, 2, 551–564.—In this interesting paper the author has verified experimentally the independence, required by the osmotic theory, of the electromotive force of various amalgam cells, of the nature of the solvent, and of the concentration of the solution required. The anomalous results obtained for the molecular weights of the alkali and alkali-earth metals as computed from the electromotive force of such amalgam cells are shown to be in harmony with Ramsay's observations on the vapor-pressure of the same amalgams. These anomalies are shown to disappear when the heat of dilution of the amalgam, which was found to be not inconsiderable, is taken into account. The heat of dilution of sodium amalgam was found to be independent of the temperature between 4° and 22°. An error relative to the electromotive force due to polyatomic zinc ions is corrected by Mr. Bancroft, *J. Phys. Chem.*, 3, 107.

The Isothermal Pressure-surface in the Case of Two Single and One Double Salt. By F. Donnan. *J. Phys. Chem.*, 2, 417–420.—A graphical discussion of the phenomena attending evaporation of a system consisting of two dissolved salts possessing one ion in common.

Solution Densities. By H. T. Barnes and A. P. Scott. *J. Phys. Chem.*, 2, 536–550.—The authors have determined the densities of a number of salt solutions at various concentrations, and have constructed plots with differences between the observed densities and the values computed on the assumption that no volume change occurs on dissolving the salt as ordinates, and weights of dissolved substance as abscissae. From the plots thus obtained the authors believe that abrupt changes of curvature are unmistakable, although they do not seem to wish to advance or advocate any "hydrate" theory in explanation. That such breaks are really present, however, does not appear probable to the reviewer, nor are they evident in the data presented.

Dissociative Power of Solvents. By Louis Kahlenberg and Azariah T. Lincoln. *J. Phys. Chem.*, 3, 12–36.—To test Nernst's rule of the relation between dissociating power and dielectric constant, the authors have studied qualitatively the relative dissociating power of some seventy-five organic liquids by means of the conductivity of salts dissolved in them. The chlorides of iron, antimony, bismuth and mercury were used as solutes. The rule was found to be verified with but few exceptions. In general the experiments show that solutions in hydrocarbons or their halogen substitution-products do not conduct; that alcoholic solutions conduct comparatively well, the power diminishing with increasing percentage of carbon in the molecule; that phenols conduct less than alcohols, ethers and acid anhydrides, slightly or not at all; aldehydes, relatively well; that nitriles and nitrogen compounds containing oxygen combined with the nitrogen both give conducting solutions, while amido compounds of the aromatic series do not. Numerous instances were noted which do not confirm Brühl's theory that solvents possessing dissociating power are unsaturated compounds, so that this theory is believed to be untenable. The paper also contains quantitative measurements of the conductivity of the chlorides mentioned above in some of the better conducting solvents, and both conductivity and freezing-point measurements on nitrobenzene solutions. The results in general indicate that cryoscopic and conductivity measurements do not in many cases agree in the case of non-aqueous solutions, and that an extension or modification of the dissociation theory may be necessary, when sufficient data to warrant general conclusions have been obtained.

Boiling-Point Curves. By E. F. Thayer. *J. Phys. Chem.*, 3, 36–40.—An extension of previous work (*this Rev.*, 4, 90) to mixtures of alcohol and chloroform, alcohol and acetone, and chloroform and acetone, is described. The chloroform-alcohol

curve possessed a minimum boiling-point at 58.5° under 732.5 mm. pressure, for a mixture containing about 7 per cent. alcohol. The chloroform-acetone curve showed a maximum boiling-point at 63.4° under 737.1 mm. pressure, for a mixture containing about 19 per cent. acetone. All mixtures of alcohol and acetone boiled between the boiling-points of their two constituents.

Determination of the Molecular Rise in Boiling-point of Liquid Ammonia. By E. C. Franklin and C. A. Krauss. *Am. Chem. J.*, 20, 836–853.—A modified form of Beckmann apparatus suitable to this low-boiling solvent was used. The molecular elevation for water and for alcohol were satisfactorily constant, both giving the same value, 3.4. Other organic solutes gave less satisfactory values, but all were of about the same order of magnitude. The salts investigated, namely, ammonium nitrate, sodium nitrate, and potassium iodide gave, in view of the high electrical conductivity of their solutions, values surprisingly low, indicating small dissociation. Metallic sodium gave a molecular elevation varying from 1.50 to 2.30, indicating a molecule containing two atoms in solution.

Some Properties of Liquid Ammonia. By E. C. Franklin and C. A. Krauss. *Am. Chem. J.*, 21, 8–14.—The authors have compared, as far as existing data permit, the various physical properties of liquid ammonia with the corresponding properties of water, thus bringing out the close relationship between these two solvents. The properties discussed are the conductivity of ammonia solutions, ammonia of crystallization, specific and latent heats, boiling-point, molecular elevation of boiling-point, dielectric constant, and molecular association.

Note on the Spectra of Hydrogen. By Theodore W. Richards. *Am. Chem. J.*, 21, 172–174.—The author points out in explanation of certain recent results of Hutton that water vapor gives the pure red spectrum of hydrogen more readily than hydrogen itself and that this spectrum is doubtless due to dissociated atoms rather than hydrogen molecules. The "white spectrum" of hydrogen, on the other hand, is obtained only in the absence of vapor; it is not to be regarded as due to impurities.

Specific Gravity of Sodium Chloride Solutions. By H. C. Hahn. *J. Am. Chem. Soc.*, 20, 621–630.—Specific gravity determinations of solutions varying in concentration from 5 per cent. to saturation at 15° C. are given to six significant figures, and several interpolation formulae with three and four constants are calculated for expressing the results.

[Contribution from the Massachusetts Institute of Technology.]

REVIEW OF AMERICAN CHEMICAL RESEARCH.

Vol. V. No. 6.

Arthur A. Noyes, Editor; Henry P. Talbot, Associate Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

GENERAL AND PHYSICAL CHEMISTRY.

H. M. Goodwin, Reviewer.

A New Determination of the Electrochemical Equivalent of Silver. By Geo. W. Patterson, Jr., and Karl E. Guthe. *Phys. Rev.*, 7, 258–282.—The discrepancy between the values of the mechanical equivalent of heat as determined by the direct and by the electrical method, led the authors to believe it might be due to errors in the standards used, in particular in the value of the ampere. A redetermination of the electrochemical equivalent was therefore undertaken. The investigation was carried out with great care in all its details, and is of particular value, as it does not involve either the acceleration due to gravity or the horizontal intensity of the earth's magnetism. The method consists essentially in balancing the electrodynamic action of the coils of a primary electrodynamometer (of special design) against the torsional moment of a phosphor-bronze wire. The measurements involved are only those of mass and time, and the authors regard their results as accurate to one part in five thousand. A silver voltameter was used with the usual precautions. The final value—the mean of four determinations—of the electrochemical equivalent of silver was found to be 0.0011192+ gram per ampere per second. This value is about $\frac{1}{9}$ per cent. greater than that generally accepted. It agrees with the average value of Pellat and Potier, and is almost identical with that given by Kahle (0.0011193 gram). Assuming the above value, the discrepancy between Griffith's and Rowland's value for the mechanical equivalent of heat disappears.

On the Density of Ice. By Edward L. Nichols. *Phys. Rev.*, 8, 21–37.—The first part of the paper contains a critical review of previous determinations of this constant, and brings out the fact that although the results of individual observers check well among themselves the agreement is not satisfactory when the results of different observers are compared. It seemed not unlikely that the nature of the ice itself was the cause of the discrepancy. To settle this point and particularly to determine the density of ice as formed in the ice calorimeter, the author made a number of careful determinations of ice from various sources, and found that the density is not the same under all circumstances, as is shown by the following values (referred to water at 0°) : Ice frozen with carbon dioxide and ether, 0.91615 ± 0.00009 ; natural icicles, 0.91807 ± 0.00004 ; newly cut pond ice, 0.91804; pond ice one year old, 0.91644.

On the Dielectric Constant and Electrical Conductivity of Liquid Ammonia. By H. M. Goodwin and M. de Kay Thompson, Jr. *Phys. Rev.*, 8, 38–48.—The di-electric constant of liquid ammonia was measured by Drude's method of electrical resonance ; and values varying from 21 to 23, according to the preparation of the ammonia, were obtained at its boiling-point (—34° C.) under atmospheric pressure. This value, which is very low compared with that of water, would seem to indicate that liquid ammonia is an exception to Nernst's Law, since reasoning from the experiments on the electrical conductivity of liquid ammonia solutions made by Cady and the authors, ammonia is probably a solvent of high dissociating power. A convenient method for measuring the conductivity of this solvent is described and results on solutions of silver nitrate are given.

On the Osmotic Pressure of Certain Ether Solutions and Its Relation to Boyle-van't Hoff's Law. By H. M. Goodwin and Geo. K. Burgess. *Phys. Rev.*, 7, 171–187.—The lowering of the vapor-pressure of solutions of naphthalene, benzophenone, and diphenylamine in ether was measured directly, by causing the solutions and the pure solvent to boil at constant temperature. Equality of temperatures was indicated by a platinum resistance thermometer placed in the boiling flasks, and pressures were measured on a mercury manometer by means of a cathetometer. From the observed vapor-pressure lowerings the corresponding osmotic pressures, P, of the solutions were computed by an exact formula which took into account the deviations of the pressure of the solvent vapor from Boyle's Law. The concentration of the solutions was reduced to mols per liter by means of specific gravity determinations, so that a direct investigation of the relation $PV = RT$ could be made. It was found that the product PV instead of being constant, diminished in all cases with in-

creasing concentration. The form of the PV curves varied with the solute, and was in general similar to the well-known curves exhibited by imperfect gases under high pressure. It would seem that each solute therefore deviates from the Boyle-van 't Hoff Law in much the same way that most gases deviate from the ideal gas laws, each substance having its own characteristic "condition-equation." Azobenzene investigated by Noyes and Abbot follows the perfect gas laws more nearly than any of the other substances thus far investigated.

ANALYTICAL CHEMISTRY.

ULTIMATE ANALYSIS.

H. P. Talbot, Reviewer.

The Determination of Potash as Perchlorate. By F. S. Shiver. *J. Am. Chem. Soc.*, **21**, 33–42.—Following a review of the various methods proposed for the determination of potassium, the author presents the results of experiments from which he concludes that the method of Caspari (*Ztschr. angew. Chem.*, *1893*, 68), as modified by Kreider (*Am. J. Sci.*, **149**, 443), will yield results equal in accuracy to those obtained by the use of platinum, in the case of mixtures free from other bases and non-volatile acids, and that it seems likely to prove satisfactory in the presence of these substances. Four procedures for the preparation of perchloric acid, those of Schlösing and of Porrey (both to be found in Grandeau's *Traité d'Analyse des Matieres agricoles*, **1**, 88–91), Caspari (*Ztschr. angew. Chem.*, *1893*, 68), and Kreider (*Loc. cit.*), are briefly described.

A New Method for the Determination of Zinc. By A. C. Langmuir. *J. Am. Chem. Soc.*, **21**, 115–118.—In the method proposed, the zinc precipitate (sulphide) is dissolved in nitric acid, the solution evaporated, and the zinc converted to oxide by ignition. It is recommended that the zinc be thrown down from a dilute solution, and that the precipitate be dissolved without washing, to avoid the usual difficulties at this point, and that the impurities in the ignited oxide be determined and deducted from the apparent weight. In the analysis of many alloys containing zinc, the solution from which the copper and lead have been removed by electrolysis, may be directly evaporated and the residue strongly ignited.

The Determination of Arsenic in Glycerine. By A. C. Langmuir. *J. Am. Chem. Soc.*, **21**, 133–136.—The glycerine is destroyed by evaporation with sulphuric and nitric acids, transferred to a Marsh generator, and the gas passed through a hard glass tube, constricted as usual, with a piece of filter-paper

moistened with mercuric chloride solution beyond the constriction to detect any escaping arseniuretted hydrogen. The portion of the tube containing the mirror is cut off and weighed. It is then cleaned, dried, and again weighed. The Gutzeit test, using mercuric chloride instead of silver nitrate, also yields good results.

Note—Drown's Method of Determining Silicon. By A. C. Langmuir. *J. Am. Chem. Soc.*, 21, 215.

Notes on the Rapid Determination of Tungsten in Steel. By George Auchy. *J. Am. Chem. Soc.*, 21, 239–245.—The author finds that the amount of ferric oxide which remains with the tungstic acid in the Blair procedure is, for the same class of steels, fairly constant, and that fusion with sodium carbonate may possibly be omitted. He finds that the amount of hydrochloric acid present when the tungstic acid is filtered off affects the determination, and that evaporation to dryness from a nitric acid solution does not always effect complete separation of the tungsten, while the separation is complete when hydrochloric acid is used. About 5 cc. of hydrochloric acid should be present when filtration takes place. In low phosphorus steels, the phosphorus may be determined as usual in the presence of the tungsten, provided the precipitate does not stand more than $2\frac{1}{2}$ hours, and an excess of ammonia is avoided. The same procedure as for steels is found to succeed with ferrotungstens.

W. H. Walker, Reviewer.

Volumetric Method for the Estimation of Boric Acid. By L. C. Jones. *Am. J. Sci.*, 157, 147–153.—In order that boric acid may be estimated volumetrically by titration with standard alkali, it is necessary to obtain it as the uncombined acid in a solution of neutral salts free from carbonic acid. The following procedure is found to fulfil these requirements more perfectly than any other method hitherto proposed, and to furnish a rapid and convenient method for estimating boric acid in any compound decomposable by hydrochloric acid. The boric acid is set free by the addition of dilute hydrochloric acid in slight excess, and 5 cc. of a ten per cent. barium chloride solution are added to combine with any carbonic acid that may subsequently be introduced with the standard alkali solution. The excess of hydrochloric acid is now destroyed by adding a considerable quantity of a solution of potassium iodate, and the iodine set free by this reaction is taken up by a dilute solution of sodium thiosulphate. The boric acid may now be neutralized by standard sodium hydroxide, phenolphthalein being used as an indicator. When the red color first appears, 1–2 grams mannite are added and the alkali again run in to a faint alkaline reaction, which if per-

manent on the addition of more mannite, may be taken as the end-point. The best results are obtained in a cold concentrated solution, and under these conditions the experimental data given show the method to be very accurate.

PROXIMATE ANALYSIS.

A. H. GILL, REVIEWER.

The Heat of Bromination Test for Oils. BY AUGUSTUS H. GILL AND ISRAEL HATCH, JR. *J. Am. Chem. Soc.*, 21, 27–29.—The calorimeter employed was double jacketted. The values obtained with the oils were compared with that obtained by brominating camphor; the results are expressed as a "specific temperature reaction," which, by multiplying by a constant, gives an iodine number which agrees well with that found in the usual way.

The Analytical Constants of American Linseed Oils. BY AUGUSTUS H. GILL AND AUGUSTUS C. LAMB. *J. Am. Chem. Soc.*, 21, 29–30.—The specific gravity, Valenta, Maumené, iodine, and drying tests of raw, boiled, and bleached oils of undoubted purity are given.

Analytical Research on Sod Oil. BY E. HOPKINS, D. L. COBURN, AND E. SPILLER. *J. Am. Chem. Soc.*, 21, 291–300.—Sod oil is the excess of oil extracted from ordinary leather in the currying process, menhaden and cod oils being used principally for this purpose, although other oils and greases are employed. It can hence have no well-defined constants, but there is little difficulty in distinguishing it from other oils. Moisture is determined by sucking air through the oil absorbed upon filter papers contained in a tube heated in an oven at 100° C. The oil is obtained by extracting this residue with 40° b. pt. gasoline; and this is followed by extraction with alcohol giving the soap; upon igniting the residue the ash is determined, and the hide fragments are ascertained by difference. Dégras former is estimated by saponifying the oil, evaporating to dryness, extracting the soap formed with water, and precipitating this with salt. The solution is filtered, the dégras former passing into the filtrate, where it is precipitated by hydrochloric acid; it is filtered off and dissolved in alcohol, the alcohol is evaporated, and the residue weighed. In addition to these determinations, tables are given showing the saponification number, mineral acid, free acid, total acid, ether number, Reichert-Meissl, iodine, and unsaponifiable numbers.

The Absorption of Methane and Ethane by Fuming Sulphuric Acid. BY R. A. WORSTALL. *J. Am. Chem. Soc.*, 21, 245–251.—The article shows that contrary to accepted facts,

both these gases are absorbed by the acid. The absorption in the case of methane was as follows: In ½ hour, 0.1 cc.; in 2 hours, 1.7 cc.; in 4 hours, 5.4 cc.; 24 hours, 6.8 cc.; and in 5 days, 11 cc. Natural gas containing 96 per cent. of methane showed an absorption varying from 0.3 to 3.3 per cent. Ethane is absorbed in a quantity varying from 3.5 to 7 per cent. The results of this investigation show that in gas analysis the gas should not stand longer than an hour over sulphuric acid, and if ethane be present not more than fifteen minutes.

A. G. Woodman, Reviewer.

Butter and Butter Adulterants. By C. B. Cochran. *J. Franklin Inst.*, 157, 85–97.—For the purpose of detecting and estimating small amounts of foreign fat in butter, the author considers the following tests most satisfactory: Direct microscopic examination of the sample by polarized light; microscopic examination of the crystals from solution in amyl alcohol, both with and without polarized light; Valenta test; Reichert number; reading of butyrorefractometer. It is concluded that if the conditions of crystallization are kept uniform the crystalline deposit obtained from the solution of pure butter-fat in amyl alcohol is characteristic of butter. Photomicrographs are given illustrating this. Results are also given of the examination of several samples of renovated butter; that is, stale butter in which the fat has been separated from the curd and water, and then emulsified with milk or buttermilk, being thus made again into butter.

Detection of Caramel in Spirits and Vinegar. By C. A. Crampton and F. D. Simons. *J. Am. Chem. Soc.*, 21, 355–358.—It has been found that fuller's earth has a greater affinity for the artificial coloring-matter of spirits than for that derived naturally from the wooden containers, and the method given for the detection of caramel is based upon the observation that a much greater percentage of color is removed from the artificially colored samples by means of this substance.

G. W. Rolfe, Reviewer.

Study of Starch Grains and Its Application. By H. Kraemer. *Am. J. Pharm.*, 71, 174–189.—This paper treats of the origin of starch in plants as indicated by the researches of the biologist and botanist, and of the physical and chemical examination of starch by the microscope. The author argues for more expert work by the botanist and biologist in food analysis.

Some Notes on the Estimation of Carbohydrates. By F. W. Traphagen and W. M. Cobleigh. *J. Am. Chem. Soc.*, 21, 369–373.—The authors describe their modification of the Feh-

ling determination. They measure the amount of precipitated copper oxide volumetrically by the permanganate method. They eliminate errors to a large extent by checking the process on solutions of similar known composition and of practically identical reducing value. Excellent results are obtained. As the Fehling determination is influenced so much by apparently insignificant points of manipulation, a more detailed description of the authors' method would be desirable.

E. H. Richards, Reviewer.

The Estimation of Nitrates and Ammonia in Water. By Frank X. Moerk. *Am. J. Pharm.*, **71**, 157–161.—Instead of using milk of alumina to remove the organic matter which interferes with the color in the phenol-sulphonic acid test for nitrates in water samples, the author makes a duplicate determination for color due to the organic matter. The remarks on ammonia determinations do not agree with the experience of the reviewer; for, while it is true that "dilute ammonium chloride will not keep indefinitely," unless under conditions of complete sterilization, it is not true "that it is useless to attempt" to free alkaline potassium permanganate "from ammonia, as it cannot be kept so." With pure reagents and suitable preparation of them, the solution, even if not at first, yet on standing, yields ammonia-free distillates.

BIOLOGICAL CHEMISTRY.

A. G. Woodman, Reviewer.

Digestive Ferments with Especial Reference to the Effects of Food Preservatives. By Henry Leffmann. *J. Franklin Inst.*, 147, 97–108.—The author has studied the action of the more commonly used food preservatives in preventing starch digestion by various enzymes. A number of qualitative experiments in which the action was followed by means of tests with a solution of iodine in potassium iodide are recorded, and in a few cases the amount of dextrose formed was determined by Fehling's solution. It was found that salicylic acid is distinctly antagonistic to the starch-converting enzymes but does not interfere very much with proteid digestion; sodium benzoate, boric acid, borax, and boroglycide do not interfere appreciably with either starch or proteid digestion; beta-naphthol interferes with the action of malt-diastase but not seriously with taka-diastase or pancreatic extract, although it interferes decidedly with the peptic and pancreatic digestion of proteids. Sodium fluoride and sodium silicofluoride offer but little hindrance to starch transformation except in the case of the pancreatic digestion.

On the Presence of Cholin and Neurin in the Intestinal Canal during Its Complete Obstruction—A Research on Autointoxication. By BEATTIE NESBITT. *J. Expt. Medicine*, 4, 1–18.—The author has carried out experiments on dogs by closing the intestinal canal by means of a ligature, the animals having been fed on yolks of eggs, which are very rich in lecithin. The contents of the intestine were examined, care being taken to avoid the decomposition of the lecithin during analytical treatment, and cholin and neurin were detected and separated by means of their platinum salts. The conclusion is reached that complete occlusion of the small intestine at its lower end causes the formation of cholin and neurin, possibly other bases also, if the food given contains any considerable amount of lecithin.

Action of Formaldehyde on Enzymes and on Certain Proteids. By C. L. BLISS AND F. G. NOVY. *J. Expt. Medicine*, 4, 47–80.—A systematic study has been made of the action of formaldehyde on various preparations of pepsin, rennin, pancreatin, ptyalin, diastase, and papaïn. The method adopted was to dissolve a certain amount of the ferment in distilled water and divide this solution into portions. A definite amount of "formalin" was added to each portion so that the liquid contained known amounts of formaldehyde, varying usually from 1 : 100 to 1 : 1000. These mixtures were allowed to stand in closed flasks at ordinary room temperature, portions being tested from time to time. Fresh, well-washed blood fibrin was used to test the proteolytic ferments, and freshly prepared starch paste for the diastatic experiments. It was found that fibrin is altered and rendered less digestible by formaldehyde; similarly, the casein of milk undergoes rapid alteration in contact with formaldehyde, and is only very slowly coagulated by rennet and is digested with difficulty by the proteolytic ferments. Pepsin was not affected even by a five per cent. solution of formaldehyde acting for three weeks, and the same general result was reached in the case of rennet. Papaïn was very quickly altered by formaldehyde even in very dilute solution, and trypsin was also altered greatly, depending, however, on the amount of organic matter that was present. Ptyalin, like the diastatic ferment of the pancreas, was found not to be destroyed by dilute solutions of formaldehyde, but was destroyed after some time by strong solutions. Malt diastase was not destroyed by formaldehyde in moderate amounts and at room temperature. The favoring action of formaldehyde on diastase is considered to be really due to the protection of the diastase against decomposition by preventing the growth of the micro-organisms.

[Contribution from the Massachusetts Institute of Technology.]

REVIEW OF AMERICAN CHEMICAL RESEARCH.

Vol. V. No. 7.

Arthur A. Noyes, Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby and M. L. Fuller; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

BIOLOGICAL CHEMISTRY.

A. G. Woodman, Reviewer.

Analysis of Commercial Vinegar. By Frank G. Ryan. *Am. J. Pharm.*, 71, 71–73.—The author presents the results of analysis of three commercial samples of vinegar obtained by the methods recommended by Smith (*this Rev.*, 4, 63).

The Adulteration of Flour. By W. A. Withers and G. S. Fraps. *N. C. Agr. Expt. Sta., Bull.* 156, 59–67.—The principal adulterant found was corn flour, which was present in sixteen per cent. of the samples.

The Alkali Soils of the Yellowstone Valley. By Milton Whitney and Thos. H. Means. *U. S. Dept. Agr., Div. of Soils, Bull.* 14, 1–37.

Commercial Fertilizers. *Conn. Agr. Expt. Sta., Ann. Rep*, 22, 1-97; *Me. Agr. Expt. Sta., Bull.* 50, 1-8; *La. Agr. Expt. Sta., Bull.* 54, 60-98; *Ky. Agr. Expt. Sta., Bull.* 79, 159-197; *Md. Agr. Coll. Quart.*, 3, 1-50; *Wis. Agr. Expt. Sta., Bull.* 73, 1-10.

Proximate Analysis of Bark of Pinus Echinata, Miller. By Chris. Koch, Jr. *Am. J. Pharm.*, 71, 164-170.—The results given were obtained on the bark of a young tree and comprise moisture and ash and the results of extraction by various solvents, following Dragendorff's scheme for plant analysis.

Dietary Studies in Chicago. By W. O. Atwater and A. P. Bryant. *U. S. Dept of Agr., Expt. Sta. Bull.* 55, 1-76.—

The general plan of the inquiry was similar to that of investigations published in previous Bulletins. The studies were chiefly made among families of the foreign-born population of Chicago, including Italians, French Canadians, Russian Jews, and Bohemians. The dietaries of three families of Americans were also studied.

E. H. RICHARDS, REVIEWER.

Report on the Investigations into the Purification of the Ohio River Water at Louisville, Ky. BY GEORGE W. FULLER. *Monograph*, 1–480. **Report of the Filtration Commission of the City of Pittsburg.** 1–393.—In several respects these two reports supplement each other and taken together mark an era in the study of water filtration problems under conditions common in America. The chemical analysis of the waters derived from two great water-sheds and the effects of the various experimental processes upon their composition, furnish valuable data for the water analyst as well as for the sanitary engineer. In both reports will be found much of interest in regard to the formation of boiler scale.

G. W. ROLFE, REVIEWER.

Sugar Beet Experiments during 1898. BY ALFRED J. MCCLATCHIE AND ROBERT H. FORBES. *Bull Ariz. Agr. Expt. Sta.*, 30, 190–225.—The results show that sugar beets can be raised, and sugar manufactured, profitably in the Salt River Valley. The fuel question is the most serious one.

Sugar Beet Investigations in Wisconsin during 1898. BY F. W. WOLL. *Bull. Wis. Agr. Expt. Sta.*,71, 3-34.—The problem of successful beet culture in the state presents no difficulties. The harvest period lasts about 55 days and can be extended a month longer by the use of silos.

The Sugar Beet. BY H. J. WATERS. *Bull. Mo. Agr. Expt. Sta.*, 45, 20–32.—The investigation of the quality of the beets raised in different parts of the state has been concluded. The results show a close agreement with those of the U. S. Dept. of Agriculture, and confirm the opinion of the latter that Missouri is not favorably located for beet culture.

Sugar Beets. BY J. T. WILLARD AND R. W. CLOTHIER. *Bull. Kan. Agr. Coll. Expt. Sta.*, 83, 2-16.—Data are so far insufficient for satisfactory conclusions.

Sugar Beet Investigations for 1898. BY J. L. STONE, L. A. CLINTON, G. W. CAVANOUGH, and A. L. KINSLEY. *Bull. Cornell Agr. Expt. Sta.*, 166, 417-468.—The data relate principally to experiments in cultivation with their effects on the quality of

the beet. Illustrations are given of the factories at Rome and Binghamton and of the apparatus used in the chemical investigation.

Sugar Beets. Notes for 1897. *Bull. Nev. Agr. Expt. Sta.* 37, 3-16.—General information for the farmer.

APPARATUS.

A. H. GILL, REVIEWER.

A Condenser for Extraction Work. BY C. G. HOPKINS. *J. Am. Chem. Soc.*, 20, 965.—This is a tubular condenser cooled internally.

On a Balance for Use in Courses in Elementary Chemistry. BY C. E. LINEBARGER. *J. Am. Chem. Soc.*, 21, 31-33.—This balance—called the Chaslyn balance—resembles in form the familiar Westphal balance for specific gravity determinations. It has a capacity of 111 grams and is sensitive to 0.01 gram when loaded. It would seem to be admirably adapted to the purpose.

Improved Apparatus. BY J. L. SAMMIS. *J. Am. Chem. Soc.*, 21, 42-45.—A burette is described and sketched with an S-shaped connection at the bottom so that it can never deliver more than 50 cc. Directions are also given for the manufacture of an electric stove for use in ether extractions.

A New Apparatus for the Determination of Volume. BY C. F. MCKENNA. *J. Am. Chem. Soc.*, 21, 50-52.—This apparatus for determining the specific gravity of powdered solids resembles a flask pycnometer with two narrow graduated tubes fused on. The substance is introduced through one of these having an expansion above closed by a tubulated ground glass stopper. The volume, before and after adding the solid, is read off on the other narrow tube, after bringing the liquid to a zero point in the former tube by exerting suitable air pressure on its surface through the tubulated stopper. No glass joints are in contact with the liquid, thus preventing leakage.

Baume's Hydrometer—American Standard. BY. S. S. EMERY. *J. Am. Chem. Soc.*, 21, 119-132.—This article consists of a table showing the comparison of Baumé degrees with specific gravities for liquids heavier and lighter than water.

A New Filtering Medium. BY G. W. SARGENT AND J. K. FAUST. *J. Am. Chem. Soc.*, 21, 287-288.—A quarter-inch layer of sand supported below by glass wool, covered with asbestos, and held in place by glass beads, is placed in a carbon funnel

and washed with nitric acid. This filter is especially applicable for manganese dioxide and ammonium phosphomolybdate. The work with them is as accurate as with paper, much more rapid, and less expensive.

A Method for Cleansing Burettes. Note. By W. Glenn. *J. Am. Chem. Soc.*, **21**, 302.—The method consists in the use of chromic acid. The reviewer having used this method for the last fifteen years can attest its efficacy, if the acid be concentrated (see also Talbot, *Quant. Analysis*, p. 58 (1897), and *J. prakt. Chem.*, 79, 117).

INORGANIC CHEMISTRY.

Henry Fay, Reviewer.

On an Isomer of Potassium Ferricyanide. By James Locke and Gaston H. Edwards. *Am. Chem. J.*, **21**, 193–206.—By treating potassium ferricyanide with potassium chlorate and hydrochloric acid Skraup obtained a red solution from which, by repeated precipitations with alcohol, he obtained an amorphous, hygroscopic powder, to which he assigned the formula $K_2Fe(CN)_6$, although he was not able to prepare it in pure condition. The authors, by modifying Skraup's conditions, have been able to obtain a pure crystallized product. Potassium ferricyanide was heated to 95° C. with hydrochloric acid and potassium chlorate until effervescence began. The solution was cooled to 20° and filtered; and to the cool filtrate slightly less than an equal volume of alcohol was added. This produced a heavy crystalline precipitate. By partial reprecipitation the crystals were obtained pure, and on analysis were shown to have the composition represented by the formula $K_3Fe(CN)_6.H_2O$. The substance is an isomer of potassium ferricyanide, and the authors propose to name it potassium β-ferricyanide. Like the ordinary salt, this isomer yields characteristic precipitates with the solutions of the heavy metals. These have, in general, the same characteristics as the salts of the normal ferricyanide, and in some cases pass over into the latter with extreme ease. The precipitate of the β-ferricyanide with silver nitrate is dark-brown and flocculent, and when heated in its mother-liquor to 100° passes over into the bright-orange of the α-ferricyanide. The potassium β-ferricyanide can readily be distinguished from the normal ferricyanide by the fact that with bismuth nitrate solutions it does not form a precipitate, while the α-ferricyanide produces an insoluble straw-colored precipitate. Stannic chloride, on the other hand, yields no precipitate with potassium α-ferricyanide, but precipitates the isomer completely. No explanation of the isomerism is offered.

On the Formation of Potassium β-Ferricyanide through the Action of Acids upon the Normal Ferricyanide. By James Locke and Gaston H. Edwards. *Am. Chem. J.*, 21, 413–418.—It has been shown that the conversion of potassium ferricyanide into potassium β-ferricyanide can be accomplished by any acid, the presence of potassium chlorate not being necessary, as was assumed in a previous paper. Potassium ferricyanide was treated with hydrochloric acid, and from time to time portions were drawn off and precipitated with bismuth nitrate. Subsequently, the percentages of cyanogen which these precipitates contained were determined by reduction with sodium amalgam and titration to potassium α-ferricyanide. The rate of conversion from β- to α-ferricyanide brought about by the catalytic action of acids seems to be directly proportional to the degree of ionization of the acid.

The Action of Metals on Nitric Acid. By Paul C. Freer and George O. Higley. *Am. Chem. J.*, 21, 377–392.—In previous papers the action of copper, lead, and silver on nitric acid of different strengths has been described. In this research the action of iron on nitric acid, and the effect of electrolytic hydrogen on it, using kathodes of copper, silver, and lead, have been investigated. When iron is dissolved in nitric acid, the reduction-products are nitrogen dioxide, nitric oxide, nitrous oxide, and ammonia. With acid of specific gravity 1.40 nitrogen dioxide and nitric oxide are obtained in proportions varying with the amounts of solvent. These differences caused by using varying amounts of solvent led the authors to the view that nitric oxide is solely a secondary product of the decomposition of the dioxide by water. As the acid diminishes in strength the variation in the relative amounts of these two products is much like that observed with copper, silver, and lead, until a specific gravity of 1.30 is reached when nitrous oxide is formed. With acid having a specific gravity of 1.25 the reaction is further complicated by the appearance of nitrogen and ammonia, the former reaching a maximum at 1.15 and then falling off, while the latter rises to a maximum at 1.05. With platinum electrodes, electrolytic hydrogen acts upon concentrated nitric acid much the same as do copper, silver, and iron, nitrogen dioxide being the principal product. Nitric oxide is produced with acid of specific gravity 1.35, and hydrogen begins to be liberated when acid of 1.30 sp. gr. is used. Small amounts of ammonia are formed only with dilute acid. The activity of electrolytic hydrogen depends, in a marked degree, upon the character of the electrode upon whose surface it is liberated. When nitric acid having a specific gravity of 1.05 is subjected to electrolysis in cells having kathodes of silver and lead, respectively, on the

surface of which kathodes there is equal current density, the reduction-products are the same ; *i. e.*, nitrogen and ammonia in approximately the same proportions. On the other hand, copper, when made the kathode of an electrolytic cell containing acid of the same strength, has a much greater energizing effect upon the hydrogen deposited upon its surface than is shown by lead under the same circumstances, and produces about three times as much ammonia as the latter. Since in the electrolysis of nitric acid the action of the metallic ions is excluded, and the reduction must be effected by the hydrogen in contact with the surface of the different metals, it follows that the widely different results obtained when lead and silver dissolve in nitric acid cannot be attributed to the hydrogen atoms alone, but must also involve the direct deoxidizing effect of the metals themselves. With concentrated, non-ionized acid the metals alone cause the change, but on dilution both metals and hydrogen cause it.

Preparation of Metallic Tellurium. By Victor Lenher. *J. Am. Chem. Soc.*, 21, 347–351.—The author has tried the different methods for the extraction of metallic tellurium from the slimes of the Baltimore Copper Works, and concludes that "reducing sugars will give a very practical method for the preparation of metallic tellurium."

Action of Hypophosphorous Acid upon Molybdic Acid. By Clarence Ebaugh and Edgar F. Smith. *J. Am. Chem. Soc.*, 21, 384–386.—A tenth-normal solution of molybdenum trioxide was reduced by hypophosphorous acid both in the presence of a definite excess of that acid and in the presence of sulphuric acid. The reduction is approximately to the oxide Mo_2O_5. Neutral solutions are not reduced.

New Method for the Preparation of Cesium. By Hugo Erdmann and A. E. Menke. *J. Am. Chem. Soc.*, 21, 259–262.—Almost the theoretical yield of cesium was obtained by heating cesium hydroxide with magnesium powder in a red-hot tube, through which a current of hydrogen was passing.

The Specific Gravity of Cesium. By A. E. Menke. *J. Am. Chem. Soc.*, 21, 420–421.—Not less than four grams of metal were weighed first in hydrogen, then under liquid paraffin. The mean of six determinations gives the value 2.400 for the specific gravity.

The Solubility in Water of Certain Natural Silicates. By George Steiger. *J. Am. Chem. Soc.*, 21, 437–439.—Certain silicates were found to give up alkali on long standing with water. The amount of alkali which went into solution was determined by means of standardized hydrochloric acid, using methyl orange as indicator.

ORGANIC CHEMISTRY.

J. F. NORRIS, REVIEWER.

Contribution to Our Knowledge of the Oil of Lemon Grass. By WILH. STIEHL. *Am. Chem. J.*, 21, 67–94.—The author shows by a review of the literature that the knowledge of the aldehydes present in the oil of lemon grass is very indefinite. Dodge (*Am. Chem. J.*, 12, 555) isolated a characteristic aldehyde, $C_{10}H_{16}O$, from the oil and called it citriodoric aldehyde. Later, Tiemann and Semmler (*Ber. d. chem. Ges.*, 26, 2708) separated geranial, and Doebner (*Ber. d. chem. Ges.*, 27, 2020) citronellal. Barbier and Bouveault (*Compt. rend.*, 118, 953, 1050) then showed that citronellal was not present in the oil, and from a study of the semi-carbazones proved that the three aldehydes present were geranial, citriodoric aldehyde, and laevo-licarhodal. And finally, Tiemann (*Ber. d. chem. Ges.*, 31, 820) asserted that the only aldehyde present in the oil of lemon grass is geranial. The author found it impossible to separate the constituents of the oil by fractional distillation, but by the action of a solution of sodium bisulphite, succeeded in obtaining three aldehydes in pure condition. By using the proper conditions, the bisulphite compound of citriodoric aldehyde remains in solution, that of geranial separates in crystals, and the addition-product of the third compound, allo-lemonal, is decomposed, setting free the aldehyde as an oil. The semi-carbazones, the α-alkyl-β-naphthocinchoninic acids, and the condensation-products with acetone of the three aldehydes, were prepared, and their physical constants determined. It is shown that geranial is not present in natural oil of lemon grass, but that it is formed from the other two aldehydes, a freshly prepared, strongly acid solution of sodium bisulphite effecting the change readily. On the other hand, when geranial is boiled with an aqueous solution of sodium acetate, it is converted into citriodoric aldehyde and allo-lemonal. The condensation-products of the latter aldehydes with acetone readily condense into ring bodies isomeric with ionone, which was obtained by Tiemann in an analogous way from geranial. They have the characteristic odor of violets. From his own work and a study of the literature the author assigns the following formulas to the aldehydes:

$$(CH_3)_2{=}C{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CHO,$$

Citriodoric aldehyde.

$$(CH_3)_2{=}C{=}CH{-}CH_2{-}CH{=}C(CH_3){-}CH_2{-}CHO,$$

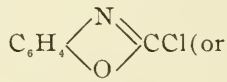
Geranial.

$$(CH_3)_2{=}C{=}CH{-}CH{=}CH{-}CH(CH_3){-}CH_2{-}CHO.$$

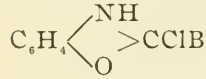
Allo-lemonal (*l*-licarhodal).

On the Constitution of the Salts of the Imido Ethers and Other Carbimide Derivatives. By Julius Stieglitz. *Am. Chem. J.*, 21, 101–111.—This paper is an introduction to two articles by McCoy and by Dains, which are reviewed below. It states briefly the reason for accepting the view that the salts of the imido ethers are formed by the addition of the acid at the double bond, the acid radicle uniting with carbon, in preference to the older view that the salt formation is due to the change in volume of the nitrogen atom.

On the Hydrochlorides of Carbophenylimido Derivatives. By Herbert N. McCoy. *Am. Chem. J.*, 21, 111–167.—Lengfeld and Stieglitz (*Am. Chem. J.*, 16, 70; 17, 98), in the course of a study of the action of phosphorus pentachloride on phenyl urethane, were led to examine the question whether the salts of imido ethers are formed by the addition of acid to the double bond between carbon and nitrogen or by direct addition to the nitrogen atom alone. If the former view is the correct one, the same compound should be formed by the action of hydrochloric acid on ethyl phenylimidobromformate and of hydrobromic acid on ethyl phenylimidochlorformate. These reactions were studied, and, although the reaction-product could not be isolated on account of its great instability, the decomposition-products were identical in both cases. In order to bring more evidence to bear on the subject, the author has investigated two analogous compounds, chlor- and brom-methenyl-*o*-aminophenol,



These compounds, when treated with hydrobromic and hydrochloric acids, respectively, yielded the same product, which from the two methods of preparation must have the formula



. The nitrate and chlorplatinate of chlormethenylaminophenol were analyzed, thus establishing the salt-like nature of the compounds, although the halogen in them was joined to carbon. A number of methods of preparing the necessary aminophenols were studied. By the action of chlorine or bromine on the compound $O.C_6H_4.NH.CS$ the corresponding chlor- or brommethenylaminophenol was prepared with excellent yield. An attempt was made to convert carbonylaminophenol, $O.C_6H_4.NHCO$, by means of phosphorus pentachloride into chlormethenylaminophenol. A mixture of compounds, from

which a very small amount of the phenol could be isolated, was obtained, thus showing that the action of phosphorus pentachloride on urethane is very complicated. In order to prepare the carbonylaminophenol required for the above experiments a new method of preparation was tried, starting from salicylic amide, based on the molecular rearrangement which the bromamides show when treated with alkalies or alcoholic sodium methylate. As a result, 3,5-dibromcarbonylaminophenol was formed, from which the bromine was readily removed by reduction. In order to establish the structure of the monohydrochloride of carbodiphenylimide, $C\langle^{NC_6H_5}_{NC_6H_5}$, a study was made of its action on benzene in the presence of aluminium chloride. Since in nearly all syntheses with the Friedel and Crafts reaction the halogen reacting is united with carbon, and since a well-defined condensation-product was obtained in the above case, the conclusion is drawn that in the hydrochloride the chlorine is joined to carbon. By a complete synthesis, in which the structure of the compounds could be followed, the product of the above reaction was shown to be either 2,4-diphenylimido-3(N)-phenyltetrahydroquinazoline or 2-phenylamido-3(N)-phenyl-4-phenylimidodihydroquinazoline. The compound exists in two forms, which are readily converted into each other by recrystallization.

On the Isourea Ethers and Other Derivatives of Ureas. By F. B. Dains. *J. Am. Chem. Soc.*, **21**, 136–192.—The work reported deals chiefly with methods of preparation of isourea ethers and a study of their physical and chemical properties. The compounds are of special interest because they contain both the amidine and imido ether groups. The presence of these two groups so modifies the compounds that they do not show a number of the characteristic reactions of imido ethers. The conclusion is drawn that the chemical behavior of the isoureas depends in a marked degree on the nature of the radicles present. The great number of facts presented makes a brief review of the paper impossible.

On the Rearrangement of Imido Esters. By H. L. Wheeler and T. B. Johnson. *Am. Chem. J.*, **21**, 185–193.—When silver formamide suspended in ether was heated in an open vessel with ethyl iodide, ethyl phenylimidoformate, $HC\langle^{NC_6H_5}_{OC_2H_5}$, was obtained. When, however, the silver salt of the amide and an excess of ethyl iodide were heated in a sealed tube at 100°, the entire reaction-product was N-ethylformanilide,

$$(C_2H_5)(C_6H_5)N.CH:O.$$

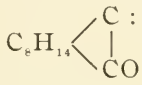
This tautomeric reaction of the silver salt is remarkable, since the difference in conditions in the two experiments is so small; and it shows clearly that synthesis cannot be relied upon as positive evidence in deciding structure. The best explanation of the facts is given by assuming the formation of an intermediate addition-product which can break down in two ways with the elimination of ethyl iodide. A rearrangement was shown also to take place with benzimidoethyl ester, which was converted into ethyl benzamide when heated with ethyl iodide at 100°.

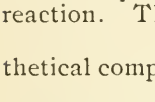
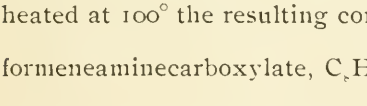
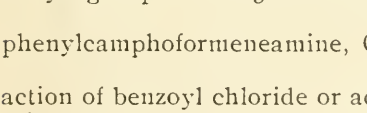
Reaction of Orthodiazobenzoic Acid with Sulphurous Acid and Copper Powder. By W. E. Henderson. *Am. Chem. J.*, 21, 206–210.—In order to test the statement made in text-books and chemical dictionaries that sulphonic acids are formed by the action of sulphurous acid on diazo compounds in the presence of copper powder, the decomposition of *o*-diazobenzoic acid sulphate under these conditions was studied. A reaction took place readily in the cold without the formation of any tarry products, and a yield of 50 per cent. of the theoretical of dithiosalicylic acid was obtained. Copper went into solution as the reaction proceeded, forming a mixture of cuprous and cupric salts, and a part of the sulphurous acid was oxidized to sulphuric acid. The reducing power of the sulphurous acid probably prevented the formation of a sulphuric acid. As the thio acid yields *o*-sulphobenzoic acid on oxidation the reaction may be of value in the preparation of sulphonic acids.

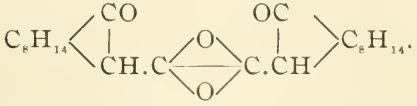
Direct Nitration of the Paraffins. By R. A. Worstall. *Am. Chem. J.*, 21, 210–218.—The author has repeated his study of the nitration of the paraffins by the method already described (*this Rev.*, 4, 87), and has extended the investigation to a number of higher paraffins. The yields of nitro and dinitro compounds from hexane were 6 and 4 per cent. respectively; from heptane, 16 and 24 per cent.; from octane, 17.5 and 25 per cent.; from nonane, 22 and 48 per cent. From decane about 35 per cent. of nitrodecane was obtained when the hydrocarbon was heated with dilute acid (sp. gr. 1.08), which was found to yield the best results. This nitro compound and the derivative of nonane were separated from the unchanged hydrocarbon by conversion into sodium derivatives and subsequent treatment of the latter with carbon dioxide. Hendecane and dodecane gave small yields of mononitro derivatives. After 75 per cent. of the original hydrocarbons had been converted into nitration and oxidation-products, the residual paraffins, when boiled with nitric acid, still gave as oxidation-products acetic, succinic, oxalic, and carbonic acids. This fact seems to show that these acids are not due to the oxidation of naphthenes or other foreign hydrocarbons, as has been claimed by other observers.

Higher Primary Nitroparaffins. By R. A. Worstall. *Am. Chem. J.*, **21**, 218–238.—The properties of the nitro compounds mentioned in the preceding review are described fully in this paper. They were converted into amines and sodium derivatives, and from the latter compounds bromnitro derivatives were prepared. The nitro compounds were shown to be primary by the action of hydrochloric acid, which converted them into the corresponding fatty acids.

The Action of Ethylic Oxalate on Camphor. IV. By J. Bishop Tingle and Alfred Tingle. *Am. Chem. J.*, 21, 238–261.—By heating aniline with camphoroxalic acid,

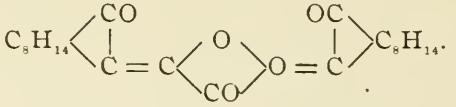


three compounds are formed, by varying the temperature of the reaction. These may be considered as derivatives of the hypothetical compound  , to which the name camphoformene is assigned. The following formulas for the compounds are deduced from their reactions: When the two substances are heated at 100° the resulting compound is aniline phenylcamphoformeneaminecarboxylate,  . By gentle heat or dilute acids this compound is converted into the corresponding acid, the aniline being split off from the carboxyl group. At 130° aniline and camphoroxalic acid give phenylcamphoformeneamine,  . By the action of benzoyl chloride or acetic anhydride on camphoroxalic acid, a substance is formed which is not changed by boiling sodium hydroxide, bromine in chloroform solution, or hydroxylamine. The compound is therefore probably not an anhydride, as was at first suggested, and the following formula is offered provisionally:



When camphoroxalic acid was boiled with acetic anhydride, a compound, in addition to the above and acetylcamphoroxalic

acid, was obtained. The formula which explains its reactions best is as follows :



When ethyl camphoroxalate is heated at 130° with aniline the product formed is phenylcamphoformeneaminecarboxylic anilide and not oxanilide, as stated in an earlier paper. By oxidizing ethyl camphoroxalate phenylhydrazide, ethyl camphoroxalate azobenzene, $C_8H_{14}\begin{cases} C : C.COOC_2H_5 \\ | \\ CO \quad N : NC_6H_5 \end{cases}$, was obtained. Attempts to condense camphor with diethyl pyrotartrate and with ethyl oxalacetate were made in hopes of getting two isomers in each case ; but no well-defined products could be isolated. Further work on the physiological action of camphoroxalic acid shows that when injected intravenously to the extent of 0.241 gram per kilo of body weight, it is practically without effect.

On a Liquid Acetylene Diiodide. By Edward H. Keiser. *Am. Chem. J.*, **21**, 261–265.—When acetylene was passed over iodine heated to 140°–160° a slow absorption took place, and the resulting reaction-product consisted of a mixture of an oil and crystals. The crystals were the ordinary acetylene diiodide. The oil, after purification by repeated freezing and liquefaction, had a definite melting-point and boiling-point, and was shown to have the composition $C_2H_2I_2$ by an analysis and a molecular weight determination. Since the liquid acetylene diiodide changes into the solid variety by standing in contact with hydriodic acid, and since it is very stable in the air, whereas the compounds $CH_2{=}CCl_2$ and $CH_2{=}CBr_2$ readily absorb oxygen, it is concluded that it is a stereoisomer of the solid diiodide.

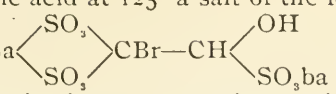
A Simple Color Reaction for Methyl Alcohol. By S. P. Mulliken and H. Scudder. *Am. Chem. J.*, **21**, 266–271.—By means of the following test the presence of one part of methyl alcohol in 10,000 parts of water or in 5 parts of ethyl alcohol can be readily shown. A hot copper spiral, which has been superficially oxidized, is dipped into the aqueous solution of the alcohol, one drop of a 0.5 per cent. solution of resorcin is added to the weak formic aldehyde solution thus formed, and the mixture is then poured slowly upon concentrated sulphuric acid. The presence of methyl alcohol is indicated by the appearance of a pure rose-red zone at the line separating the denser and lighter layers. In and above this colored band is suspended a white or

pinkish coagulum, which, after long standing, increases notably in color intensity, and finally separates and rises in purplish-red flocks. The test was applied to a large number of substances. The only other compounds studied which give colorations in the least resembling that caused by methyl alcohol, are secondary and tertiary butyl alcohols, dimethylethylcarbinol, and formic acid. With these compounds, however, no confusion need arise for the coloring-matter does not separate and rise to the surface in solid flakes.

Reactions for the Detection of the Nitro Group. By S. P. Mulliken and E. R. Barker. *Am. Chem. J.*, 21, 271–276.—The first test described depends on the fact that all nitro compounds when dissolved in dilute alcohol are reduced, in the presence of calcium chloride, by zinc dust to hydroxylamines. The test is applied by dissolving three drops of the nitro body in 3 cc. of 50 per cent. alcohol, adding five drops of a 10 per cent. solution of calcium chloride, a small amount of zinc dust, and heating till violent boiling begins. The presence of a hydroxylamine derivative in the filtrate from the reaction mixture is shown by pouring a few drops of the clear liquid into a strongly ammoniacal solution of silver nitrate in dilute alcohol. The only important classes of nitrogenous compounds which do not reduce ammoniacal silver nitrate in the cold but which effect the reduction after treatment with zinc dust are nitroso, azo, and azoxy bodies. The second test depends on the fact that nitro compounds in the presence of iron and hydrochloric acid oxidize a mixture of equal parts of aniline, *o*-toluidine, and *p*-toluidine to rosaniline. Three drops of the nitro compound are boiled three minutes with 2 cc. of the above mixture, 2 cc. of distilled water, 2 cc. of concentrated hydrochloric acid, and 1 gram of iron filings. A few drops of the reaction-product are poured into dilute acetic acid in order to bring out the clear magenta color. The test is not very successful with trinitro derivatives, and is given by all compounds which contain oxygen linked to nitrogen. Iodoso- and iodobenzene give purplish-red solutions.

Aliphatic Sulphonic Acids. III.—(1) Bromethylenesulphonic Acid. By Elmer P. Kohler. *Am. Chem. J.*, 21, 339–370.—When bromine reacts with ethylenesulphonic acid dissolved in water, fuming hydrobromic acid, or glacial acetic acid, the first result is the substitution of bromine for the α-hydrogen atom, which takes place at 0°. The (1)-bromethylenesulphonic acid so obtained is extremely unstable. When a moderately concentrated solution of the acid is heated to boiling and neutralized with a soluble carbonate, from 35 to 50 per cent. of it is decomposed—the bromine and sulphoxyl grouping being split off as bromide and sulphite. If an equally strong solution of the

potassium salt is boiled with the same carbonate, there is a rapid addition of water but no elimination of sulphite. Nascent hydrogen replaces the bromine in bromethylenesulphonic acid with hydrogen, potassium hydroxide with hydroxyl, and mercuric chloride with chlorine, but the acid does not lend itself to double decomposition, and it is impossible to link two molecules by eliminating the halogen by silver. (1)-Bromethylenesulphonic acid differs from the analogous carbonic acids in that, like ethylenesulphonic acid, it shows no tendency to combine with two atoms of the same kind or with two similar groups. Nascent hydrogen only replaces the bromine with hydrogen; and bromine, chlorine, and hypochlorous acid oxidize it in the cold. On the other hand, it combines with dissimilar atoms or groups far more readily than unsaturated carbonic acids. Water, hydrobromic acid, sulphuric acid, acetic acid, and acid sulphites are all slowly taken up in the cold. In all these cases the negative component of the molecule goes to the (2)-position. The (1,2)-oxyethanesulphonic acid obtained in this way is bromisethionic acid. A comparison of it with isethionic acid shows an important difference in the formation of anhydrides and in the behavior towards oxidizing agents. Where isethionates are heated they lose a molecule of water for two molecules of salt and pass into diisethionates. The salts of the brom-acid behave in the same way, but they are also capable of forming anhydrides from one molecule of salt. With potassium permanganate isethionates always give stable sulphoacetates. The same oxidizing agent completely destroys brom-isethionates, the products being carbon dioxide, water, hydrobromic acid, and sulphuric acid. Bromine, chlorine, and hypochlorous acid act in the same way on the brom acid, whereas nitric acid gives oxalic acid, silver oxide gives glycolic acid, and barium manganate which is kept neutral with a current of carbon dioxide gives bromsulphoacetic acid. (1,2)-Dihalogen ethanesulphonic acids were obtained by the action of phosphorus pentachloride on bromoxyethanesulphonic acid, and by the addition of hydrobromic acid to bromethylenesulphonic acid. The salts of these acids are quite stable. By prolonged boiling with water, alkaline carbonates, acetates, or silver oxide, the (2)-halogen can be completely replaced by hydroxyl, while the (1)-halogen and the sulphonic acid group are left intact. The alkalies and barium hydroxide instantly attack the (1)-halogen in the cold, splitting off halogen and the sulphonic acid group, and leaving aldehydes or their polymeric products. With zinc or magnesium both of the halogen atoms can be readily eliminated, leaving an unsaturated acid. Bromethylenesulphonic acid unites with one molecule of sulphuric acid at 80°, forming bromethylenedisulphonic acid. If the barium salt of the acid is heated with a large ex-

cess of sulphuric acid at 125° a salt of the following composition is obtained :  .$2H_2O$. The acid is a bromine substitution-product of an acid which has already been obtained by the action of acid sulphites on chloral.

On the Hydrolysis of Acid Amides. By Ira Remsen. *Am. Chem. J.*, **21**, 281–284.—This paper is an introduction to one that follows by E. E. Reid (see next review), and points out the effect that a group has on another in the ortho position to it. The fact that *p*-sulphaminebenzoic acid is not acted upon when boiled with dilute hydrochloric acid, whereas benzoic sulphinide is first converted into the corresponding ortho acid and then into the acid ammonium salt of *o*-sulphobenzoic acid by the same reagent, led to a systematic study of the hydrolysis of acid amides.

Experiments on the Hydrolysis of Acid Amides. By E. Emmet Reid. *Am. Chem. J.*, **21**, 284–349.—The rate of hydrolysis of the amides studied was determined by drawing off samples of the solutions in which the hydrolysis was being effected by dilute acids or alkalies at definite intervals, and estimating the nitrogen present in the form of ammonia and that in the unchanged amide. Freshly precipitated magnesium hydroxide proved to be an excellent reagent to distinguish between the two forms of nitrogen. It readily set free ammonia from the ammonium salt, but did not affect the amide. After the ammonia had been distilled off sodium hydroxide was added and the nitrogen in the amide was determined. The experimental details were carefully worked out, and consequently very trustworthy results were obtained. Twenty-two amides were studied, which included the nitro, chlor, brom, iod, hydroxy, amido, methoxy, and ethoxy derivatives of benzoic acids. The results obtained with the meta- and para-substituted benzamides go to show that groups in these positions usually exercise some, though not a very marked, retarding influence on the rate of hydrolysis. The rate does not vary regularly with the change in molecular weight. The nitro group in the para position causes a very marked increase in the speed of hydrolysis. The experiments with the ortho-substituted benzamides all show that groups in this position exert a remarkable protective influence on the amide group, the reaction-constant for the ortho acids being roughly about one-tenth that of the meta acids. With similar groups this influence varies roughly with the weight of the group, but otherwise it seems to depend more upon the nature of the group than its weight. Methyl protects far better than chlorine or even than the methoxy group. The nitro group is remarkable in its

protective power, being twice as efficient as iodine. The methoxy and ethoxy groups have far less effect than hydroxyl.

Emetine Octoiodide and the Extraction and Estimation of Alkaloids Generally. By H. M. Gordin and A. B. Prescott. *J. Am. Chem. Soc.*, 21, 231–239.—A detailed description of a new method of extraction of alkaloids from drugs, and directions for applying the authors' volumetric method for their estimation are given fully. By pouring an acidulated solution of emetine into an excess of iodine dissolved in potassium iodide, a periodide was precipitated which probably had the formula $C_{28}H_{40}N_2O_5.HI.I_7$.

Coumarin and Vanillin, Their Separation, Estimation, and Identification in Commercial Flavoring Extracts. By William H. Hess and Albert B. Prescott. *J. Am. Chem. Soc.*, 21, 256-259.—Coumarin and vanillin are separated from an aqueous solution by extraction with ether which is then shaken with dilute ammonia. The coumarin remains dissolved in the ether while the vanillin goes into solution in the ammonia, from which it can be separated by means of dilute acid.

The Oxidation of Formic Aldehyde by Hydrogen Peroxide. By J. H. Kastle and A. S. Loevenhart. *J. Am. Chem. Soc.*, 21, 262–276.—The effect of temperature, sunlight, acids, and bases on the reaction stated in the title was studied. The rate of the reaction increases very rapidly with rise in temperature. The accelerating effect of light is greatest at low temperatures, gradually diminishing with increasing temperature until at about 90° the effect disappears. The effect of acids is to increase the speed of the reaction but not to such an extent as has been observed in the case of other oxidation reactions which have been studied. Bases cause the oxidation to take place so rapidly that the reaction could be studied at ordinary temperatures only.

Upon the Action of Sulphuric Acid on Thymol, III. By James H. Stebbins. *J. Am. Chem. Soc.*, 21, 276–281.—The principal product of the action of 66° sulphuric acid on thymol, at the temperature of the water-bath, was thymol-*p*-sulphonic acid. A very small amount of a second compound, which was probably a disulphonic acid, was also obtained.

Observations on Derivatives of Aconitic Acid. By D. C. Hanna and Edgar F. Smith. *J. Am. Chem. Soc.*, 21, 381–383.—By distilling 90 grams of aconitic acid with phosphorus trisulphide about 0.7 gram thiophtene was obtained. Triethyl aconitic ester was produced by heating triethyl citric ester with phosphorus trichloride.

[Contribution from the Massachusetts Institute of Technology.]

REVIEW OF AMERICAN CHEMICAL RESEARCH.

Vol. V. No. 8.

Arthur A. Noyes, Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby and M. L. Fuller; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

GEOLOGICAL AND MINERALOGICAL CHEMISTRY.

M. L. Fuller, Reviewer.

Geology of Certain Counties of Iowa. By A. G. Leonard, Samuel Calvin, and H. Foster Bain. *Iowa Geol. Survey*, *Ann. Rep.*, 8, 51–366.—The physiography, stratigraphy, and geological structure of each county is described, and a discussion is given of the economic products, accompanied by a number of analyses.

Properties and Tests of Iowa Building Stones. By H. Foster Bain. *Iowa Geol. Survey*, *Ann. Rep.*, 8, 367–416.

On the Phenocrysts of Intrusive Igneous Rocks. By L. V. Pirsson. *Am. J. Sci.*, 157, 271–280.—The objections to the hypothesis of an intratelluric origin of the phenocrysts are discussed, and evidence pointing to an origin by crystallization "in place" is presented. The supposed manner in which the development takes place is as follows: As the temperature of an intruded aqueous magma falls, centers of crystallization are set up, the intervals of crystallization of the component minerals becoming progressively shorter as the magma becomes viscous from the escape of the water-vapor. Thus, while the earlier, or ferro-magnesian, components may reach considerable size, the crystals of the later components are comparatively small. In the case of recurrent phenocrysts it is supposed that the most abundant components tend to set up centers of crystallization before their normal periods, the rest of the process continuing as before.

On the Occurrence, Origin, and Chemical Composition of Chromite. By J. H. Pratt. *Am. J. Sci.*, 157, 281–286.—The usual mode of occurrence of the chromite of North Carolina is in the form of rounded masses of varying proportions in the peridotite near its contact with the inclosing gneiss. Its basic character is an indication of its insolubility in the peridotite magma; hence it would have been among the first of the minerals to solidify. Its relation to the inclosing rock confirms this view. With two exceptions, all analyses known show the presence of magnesium and aluminum, and the author concludes that chromite is really a combination of the three isomorphous molecules, $FeO.Cr_2O_3$, $MgO.Cr_2O_3$, and $MgO.Al_2O_3$. The $MgO.Al_2O_3$ is represented by the mineral spinel, and the discovery of $MgO.Cr_2O_3$ as a definite mineral may be expected.

Some Rock-forming Biotites and Amphiboles. By H. W. Turner. Analyses by W. F. Hillebrand, H. N. Stokes, and William Valentine. *Am. J. Sci.*, 157, 294–298.—The paper includes descriptions and very complete analyses of biotite from granite, quartz-monzonite, and gneiss from the Sierra Nevada region, and of the amphibole of gabbro and quartz-monzonite from the same locality. Complete analyses of most of the rocks are also given. The work was executed in the laboratory of the U. S. Geol. Survey, the object being to furnish a basis for calculating the molecular composition of the rocks in question.

On the Occurrence of Paleotrochis in Volcanic Rocks in Mexico. By Henry S. Williams. *Am. J. Sci.*, 157, 335–336.—More or less regularly striated biconical forms resembling the supposed coral Paleotrochis of Emmons was found by Alfred Dugès in the volcanic rocks of an old eroded cone northeast of Guanajuato in the Santa Rosa Mountains. The explanation is suggested that in the upward passage of superheated siliceous waters through the rock a point might be reached where a sudden loosening of the texture would permit a rapid upward radiation of the heat, while below the point the temperature would remain nearly constant for long periods. Deposition would take place wherever a cavity existed, but the supply of silica would be furnished only as it was abstracted by solidification. It is considered that the cavity would be increased in size by the crystallization, and that "the accretion-surface would increase with the lengthening of the cone by the separation of the apices of the cones, consolidation taking place at the point of meeting of the solidified silica with the water, and the water reaching that point slowly."

Origin of Paleotrochis. By J. S. Diller. *Am. J. Sci.*, 157, 337–342.—A summary of the reviews of previous writers, and descriptions of both the macroscopic and microscopic characters of specimens from Mexico (see preceding review), and from the San Christian Gold Mine of North Carolina are given in some detail. In both cases the Paleotrochis occurred in igneous rock, the analysis of the North Carolina type, which is given in full, indicating a rhyolite. The more perfect Paleotrochis are composed of granular quartz and were deposited within the more or less elongated spherulites with which the rock abounds, but whether this deposition followed soon after that of the spherulites in the course of consolidation, or took place in hollow spherulites (lithophysae), or were the result of subsequent alteration, is not clear. The biconical forms suggest that they may have originated as two spherulitic sectors, of which the apices were the centers from which the growth started.

On the Association of Argillaceous Rocks with Quartz Veins in the Region of Diamantina, Brazil. By Orville A. Derby. *Am. J. Sci.*, 157, 343–356.—The paper discusses in detail the characters and probable origin of certain more or less strongly decomposed rocks of the Diamantina district. An exhaustive analysis of a cyanitic schist from the region in question, made by W. F. Hillebrand, is included.

Goldschmidtite, a New Mineral. By William H. Hobbs. *Am. J. Sci.*, 157, 357–364.—The new mineral, to which the name of goldschmidtite has been given by the author, is a brittle, silver-white substance, having a hardness of about 2 and a specific gravity of 8.6. It is found in the form of minute columnar monoclinic crystals attached to the chalcedonic coatings of the fragments of a brecciated igneous rock of the acid type occurring at the Gold Dollar Mine, Arequa Gulch, Cripple Creek. The analysis shows the presence of 31.41 per cent. of gold, 8.90 per cent. silver, and 59.64 per cent. tellurium, corresponding to the formula Au_2AgTe_6, and giving it a position intermediate between calaverite and sylvanite. Twenty-two crystal forms were recognized, ten of which are also recognized in sylvanite, to which the new mineral is most closely allied.

On a Hydromica from New Jersey. By F. W. Clarke and N. H. Darton. *Am. J. Sci.*, 157, 365–366.—This golden-bronze mineral, which differs widely from any hitherto-described mica, is found mainly as thin coatings in veins of calcite adjacent to the diabase wall rock at Rocky Hill, N. J. The analysis indicates an orthosilicate of the formula

$$(KH)_{68}(MgFe)_{24}(AlFe)_{51}(SiO_4)_{67}.28H_2O,$$

pointing to a mixture of muscovitic ($R'''(SiO_4)_3R'_3$) and phlogopitic ($R'''(SiO_4)_3R''_3H_3.3H_2O$) molecules in the ratio of 9 to 5.

METALLURGICAL CHEMISTRY.

H. O. Hofman, Reviewer.

Porous Castings and Occluded Gases. *J. Am. Foundrymen's Assoc.*, 6, 18.—The paper discusses the effects of hydrogen and sulphur dioxide in castings of brasses and bronzes and of carbon monoxide in castings of steel and suggests some methods for getting rid of occluded gases.

Phosphor Bronze—a Description of Its Characteristics and Methods of Manufacture. By L. S. Smith. *Am. Eng. and R. R. J.*, 73, 147–149.—The author distinguishes high tensile bronze, the alloy of copper, tin, and phosphorus, and bearing bronze, the above alloy to which lead has been added. He gives a brief history of the manufacture, the compositions and specifications of the alloys, discusses the action of phosphorus in bronze, the foundry treatment of the alloy, and the method of introducing the phosphorus.

The Progress of Metallography in 1898. By A. Sauveur. *The Metallographist*, 2, 1–8.

The Microstructure of Bearing Metals. By G. H. Clamer. *J. Franklin Inst.*, 146, 138–153.—The two leading requirements of bearing alloys, *viz.*, good antifriction and good bearing qualities, depend not only upon the chemical composition but also upon the structure of the alloy. The author discusses three white-metal alloys (having the composition, Pb, 80.00; Sn, 4.75; Sb, 15.00; Bi, 0.25: Pb, 70.00; Sn, 10; Sb, 20: and Sn, 80.00; Sb, 10.00; Cu, 10.00), miscellaneous alloys (with over 60 per cent. of copper, the rest consisting of Zn, Sn, Pb, Sb, etc.), a copper-tin alloy (composed of 7 parts Cu to one part Sn once used in railroad cars, but now abandoned), and phosphor bronze (Cu, 78.72; Pb, 9.89; Sn, 10.58; P, 1.04, which, after remelting, gave Cu, 80.39; Pb, 8.35; Sn, 10.40; P, 0.87), with copper-tin-lead alloys, the last two being commonly used for locomotive journal bearings.

A Study of the Microstructure of Bronzes. By A. E. Outerbridge, Jr. *J. Franklin Inst.*, 147, 18–31.—The author having examined microscopically a large number of specimens of bronze cut from small castings found that the appearance of the etched surfaces varied greatly with the length of time that they had been exposed to the acid and suggests that a uniform system should be adopted so as to permit satisfactory comparisons.

The Reduction Works for Silver Ores at Aduana, Sonora, Mexico. By M. T. Armas. *J. Franklin Inst.*, 146, 293–302; 349–357.—The paper is a description of the metallurgical treatment of the complex ores at the works. The ores are of four kinds: 1. Smelting ores, argentiferous gray copper with some blende and galena: SiO_2, 36.2; Cu, 11.4; Pb, 9.8; CaO, 1.8; Fe, 2.1; S, 10.8; Zn, 11.5; Sb, 6.3; As, 5.2; As_2O_3, 1.2; Ag, 2.4. 2. Black ore, a complex mixture of galena, blende, copper glance, chalcopyrite and sulphantimonides and arsenides with more or less silver: SiO_2, 41.4; Cu, 11.4; Pb, 9.8; CaO, 0.8; Fe, 3.1; S, 11.3; Zn, 13.2; Sb, 4.2; As, 3.3; Ag, 1.07. Also plomores, similar to black ore, only richer in lead: SiO_2, 33.2-33.0; Pb, 30.6-28.1; Cu, 6.8-8.0; Zn, 11.5-16.3; S, 12.2-11.1; Sb, 2.1-1.2; As, 2.6-0.9; Ag, 0.60-0.88. 3. Milling ores, siliceous, especially rich in blende: SiO_2, 66.20; Al_2O_3, 0.30; Fe, 4.00; CaO, 1.80; MgO, trace; Zn, 9.35; Cu, 3.82; S, 6.76; Pb, 4.60; Sb, 1.20; As, 0.84; Ag, 0.22 (ranging from 48 to 72 oz. per ton). 4. Concentrating ores, mixed sulphides assaying 23 oz. silver per ton. The concentrates obtained by wet-stamping and passing over Frue vanners with corrugated and plane belts, have the following composition: SiO_2, 12.0; Pb, 19.1; Cu, 12.1; S, 22.2; Zn, 21.0; Al_2O_3, 1.2; CaO, 0.9; Sb, 3.2; As, 4.1; Fe, 2.9. There are two methods of treatment, chlorodizing roasting followed by leaching with hypo salt and matting with incidental liberation of lead to be cupelled and serving to work up the sulphides from the leaching plant. The hand reverberatory furnace used for chlorodizing has four hearths, 4×9 feet, the ore charge of 1200 lbs. remains 2-3 hours on a hearth, the salt (4–8 per cent.) is added on the last hearth two hours before drawing. An addition of one per cent. pyrite greatly facilitates the chlorodizing roast of ores low in sulphur, the chloridation assay giving 97.5 per cent. soluble silver. The 9 leaching tanks of the plant are 20 feet in diameter and 5 feet deep; they have a gravel filter one foot deep, and hold each 37–45 tons of ore. In base-metal leaching the wash-water is at first admitted from below and the soluble salts are removed in 15–24 hours. The wash-water is freed from copper and silver by being passed over matte, the copper content of which is raised thereby from 35 to 40 per cent. The silver solvent is a mixture of sodium and calcium hyposulphite of a strength of 0.55–0.60 per cent., the rate of leaching is $2\frac{13}{16}$ in., the average time required for a charge 14 days, and the assay of the tailings 2.57 oz. silver per ton. The three precipitating tanks are 12×6 feet and have each a capacity of 678 cu. ft. The precipitant is calcium polysulphide. It is prepared by filling one tank (8 ft. in diameter by $6\frac{1}{2}$ feet in height) 1 foot deep with water, boiling with live steam, adding first burnt lime (100) then sulphur (70),

boiling for 5–6 hours, and decanting the solution (6213 liters) with a storage tank. The residue is again treated with water and steam, but a smaller quantity of reagents (lime 79 : sulphur 56) is added, giving a second solution of the same strength and quantity as the first. The residue from the second boiling is discharged onto the sand filter of a second vat (6 ft. diameter by 6 ft. in height) and allowed to dry. It is then exposed to the oxidizing action of the air and leached with water, giving a calcium hyposulphite solution of a strength of 6.2 per cent. The sulphides from the precipitating vats (containing 24 per cent. silver and 31 per cent. sulphur) are treated with lime and boiled to extract the free sulphur before they are worked on the lead-bath of an English cupelling furnace. Treating, for example, 11.75 lbs. sulphides with lime and steam for 1 hour gave 54 liters calcium polysulphide of 2° B., containing 5.380 grams sulphur per liter. The concentrates are formed into bricks, 8×3×1 inches, with a clay-like mass of weathered rhyolite (SiO_2, 54.0; Al_2O_3, 18.6; Fe_2O_3, 15.4; CaO, 2.2; H_2O, 8.6) and charcoal fines, in the proportion, clay 13 per cent., charcoal 8 per cent., and concentrates 79 per cent. The bricks are air-dried, carefully stall-roasted and smelted for a matte to be concentrated to 40 per cent. copper by retreatment. The argentiferous lead which separates out is cupelled in an English cupelling furnace. The test of the cupel, 46×59 inches, is filled with 1579 lbs. of a mixture of 100 limestone (SiO_2, 10.0; Al_2O_3, 0.8; Fe_2O_3, 3.4; CaO, 47.0; H_2O, 1.8; CO_2, 37.0) and 46 weathered rhyolite (SiO_2, 54.0; Al_2O_3, 18.6; Fe_2O_3, 15.4; CaO, 2.2; H_2O, 8.1) crushed to pass a 4-mesh sieve. It holds 3500 lbs. lead; the blast-pressure is 7 oz. per square inch; the loss in silver in cupelling is only 0.7 per cent., the silver bars being brought to a fineness of 990.

How to Build and Operate an Arrastra. By E. L. Ballou. *Min. Sci. Press*, 78, 32–34.—This is an illustrated description of the method of erecting a water-power arrastra and of the mode of operating.

The Arrastra and the Stamp Mill. By M. F. Leech. *Eng. Min. J.*, 67, 466.—The arrastra has always been considered a primitive gold amalgamating apparatus suited for the prospector or the small operator. If the ore is crushed sufficiently fine before it is charged into an arrastra, the working capacity of the latter is greatly increased. Thus at Silver City, Idaho, a 5-feet arrastra treats in 24 hours 5 tons of stamped ore. Three 10-feet arrastras set tandem could treat in 24 hours 30 tons average ore rolled to pass a 10-mesh sieve. Setting arrastras in tandem increases the crushing capacity because the drags and their motion can be adapted to the different kinds of work that the three

successive mills have to do. The tailings from such a tandem mill can be readily run to a concentrating machine by thinning the pulp in the last arrastra. If roasted ores are to be amalgamated, a mechanical roaster can discharge continuously hot ore into the first arrastra and any imperfection in the roast be corrected by concentrating after the pulp leaves the third arrastra.

Temperature of Battery Water. By W. F. Drake. *Min. Sci. Press*, 77, 556.—The author found that if in milling gold ore the temperature of the battery water went below 50° F. it had to be heated, as otherwise the yield in gold would diminish, the best results being obtained with water of 80°-90° F. A smaller amount of quicksilver was then found to be necessary than when the water was cooler.

Temperature of Battery Water. By Mine Superintendent. *Min. Sci. Press*, 77, 505.—It is usually admitted that a temperature of 60°–70° F. is best for the water used in battery amalgamation of gold ores, although some millmen claim that it is just as well to have it ice-cold. The paper is a record of some instances in which water above 70° F. gave better results than when below. Thus, in one mill the saving of gold was 90 per cent. with water at 80° F., and only 80 per cent. when at 60° F. The warmer water seemed, however, to increase the greenish film of oxidized copper on the plates, but the squeezed amalgam was richer in gold. At the Virtue mine, Baker City, Ore., battery water at 90° F. had to be used; the saving of gold was very high, 90 per cent. by amalgamation with ore running $12–$16 in gold; less quicksilver was used than with cold water, in fact the amalgam was kept so hard as to have a frosty appearance. This was found to be necessary to prevent any quicksilver from draining off, which probably is the greatest objection to the use of warm water.

The Utica Mine Chlorination Plant. By T. N. Smith. *Eng. Min. J.*, 57, 467–468.—The ore treated is a concentrate containing 33 per cent. iron, 37 per cent. sulphur, and 30 per cent. calcium carbonate. It is roasted in six long-hearth continuous hand-reverberatory furnaces, 12×80 feet. A furnace holds 4 charges, each weighing 2400 lbs. with 10 per cent. moisture. In the furnace, which has a flat bottom, the charges are kept 2 feet apart. The 30 feet of the hearth near the fire bridge form the finishing hearth. In the rest of the furnace each ore-charge occupies about 15 feet of the length of the hearth. Supposing the finishing hearth to be empty and the sulphur of the charge next to it to be burning, this charge will be spread over the 30 feet of the finishing hearth, the working doors kept open, and no wood burned in the fireplace for about 4 hours. When all the sparks

have disappeared, the back half of the charge is moved forward 15 feet and spread over the front half; the fire is started again and kept going for two hours. In the meantime the space of 15 feet made vacant by one-half of the finishing charge is filled by moving down the next following charge, etc. After 2 hours' heating, the finishing charge will have become red-hot and will be drawn, the sulphur of the next following one will have begun to burn when 40 lbs. of salt are added to convert calcium carbonate into chloride and thus reduce later on the consumption of chlorine. When the finished charge has been drawn, the next following one, occupying 15 feet of the finishing hearth, is spread over its entire length of 30 feet. Every 6 hours a charge is drawn and given. The men work in 6-hour shifts, one man working 8 hours to assist in drawing, moving, and charging. A charge of roasted ore, after having cooled, is wetted with 12½ lbs. concentrated sulphuric acid (diluted with 12 per cent. water), mixed and shoveled into a heap in front of a leaching vat. The four leaching vats, made of 2-inch pine, are 8 feet 6 inches in diameter, 3 feet 6 inches high, and have a 6-inch gravel filter. Laths 1½-inch square are placed on the bottom 1 foot apart, across these 6-inch strips, 1 inch apart, next follow flat pieces of rock, then gravel 1 inch in diameter and from 6 to 7 fine sizes of sands; the last one is covered with 4-inch strips used as a shoveling floor, the spaces between them being filled with fine sand. The ore is screened into the vat through a 9-mesh sieve, the gas is admitted for 6–8 hours through three openings in the bottom. The gas is produced in three lead generators, taking together 90 lbs. pyrolusite, 100 lbs. salt, and 200 lbs. concentrated sulphuric acid. After remaining in gas for 48 hours, the ore is leached with water to about fill a settling tank, 8 feet in diameter and 4 feet deep, after which ferrous sulphate will give no reaction for gold; the discharge-hose is now hung up and the tub allowed to stand until next morning, when 1 ton of water is run through, which finishes the leaching. To the gold solution in the settling vat are added 15 lbs. sulphuric acid to separate some sulphates; it is then run into the precipitating vat and the gold precipitated with ferrous sulphate. The gold is given 48 hours for settling, which is assisted by adding 1 oz. of barium chloride, the barium sulphate formed carrying down any float-gold. The extraction of the gold is 90 per cent., its fineness 0.997. Recently liquid chlorine has been substituted for 90 per cent. of the gaseous chlorine, it taking 20 minutes to admit it. The liquid chlorine is received in drums 5 feet long by 10 inches in diameter; a drum weighs 300 lbs., holds 115 lbs. liquid chlorine (under a pressure of 200 lbs.), and replaces 972 lbs. pyrolusite, 1080 lbs. salt, and 2160 lbs. sulphuric acid. The cost of working per ton of concentrates is with gaseous

chlorine alone $7.80, with liquid and some gaseous chlorine $6.90.

The Lixiviation of Slimes. By A. James. *Eng. Min. J.*, 67, 378.—The paper makes a comparison between leaching slimes by the use of a filter-press at the Kalgoorie mines, Western Australia, and leaching by circulation of pulp with transfer from vat to vat by means of centrifugal pumps followed by decantation and washing at the Witwatersrand mines, South Africa. In general, it may be said that the filtering process requires less water, but the extraction is less perfect and costs more than the circulation process. With sufficient water, as in the South Africa gold districts, the latter process is the only one used; in the arid region of Kalgoorie the dirth of water has so far made filtering the leading process.

The Electro-Zinc Process, and Experimental Researches Which Led to Its Development. By W. Bettel. *Min. Sci. Press*, 78, 178; 208.—The author describes some experiences that he had in treating fine gold-bearing slimes with potassium cyanide and a filter-press. The slimes containing about 0.3 oz. gold per ton were pulped with a 0.2 per cent. cyanide solution to which potassium permanganate (0.1 lb. per ton of dry slimes) had been added as an oxidizing agent, passed through a Johnson filter-press with 24-inch frame, and then washed. The extraction of gold based on the assay of the tailings was 98.2 per cent. The author has improved the ordinary Johnson press so that by a single movement the different plates are separated a sufficient distance to allow a rapid removal of the slime cakes. In searching for means to clarify dilute cyanide solutions from slimes so as to be able to decant them, the author found that hydroxides which form insoluble compounds with silica, such as those of calcium, strontium, and barium, worked satisfactorily. In large-scale work, of course, only calcium hydroxide is available. In following this method of clarifying, he found that float-gold (Zsigmondi's colloidal gold) was carried down with the slimes, *i. e.*, gold so finely divided that when prepared chemically it would give water a pink color. Tests showed that a solution which, after passing through Pasteur-Chamberland filtering candles, would assay 1 grain gold per ton would, after clarifying with calcium hydroxide, assay only 1½ grains. In order to determine by a quick assay the value of gold in dilute cyanide solutions, the author took samples of from 200 to 1000 cc., shook them for 20 minutes in stoppered flasks with from 5 to 20 cc. sodium amalgam containing 0.1 per cent. sodium, treated the quicksilver separated from the solution with nitric acid until a small globule remained and parted this carefully. Comparative tests proved that the method was accurate to 98–

95 per cent. with a solution containing 1 oz. to 5 dwts. of gold, to 95–90 per cent., with a solution of 5 to 1 dwt.; and to 90–80 per cent. with a solution of 1 to 0.1 dwt.; with the last solution it was advisable to take 2500 cc. and 10 cc. sodium amalgam. By applying the necessary corrections values were obtained which were accurate within 2 per cent. of the truth. In experimenting on the electrical precipitation of gold from cyanide solutions the author tried sodium amalgam, which worked very well at first, only 1.5 grains gold per ton being left in a solution containing 1 oz. per ton, but the rapid decomposition of water accompanied by the oxidation of the zinc soon rendered the reagent useless for a weak solution. The idea of producing a galvanic couple by coating the usual zinc shavings with copper, lead, bismuth, and silver, respectively, as suggested by Gladstone and Tribe by dipping them into the solutions, was carried out in a 100-ton experimental plant. As long as the solutions were clear and the couples clean, the precipitation was most satisfactory; even charcoal did satisfactory work as long as the hydrogen remained occluded in its pores. After some time, however, the precipitation began to slacken and then to stop, the causes of which were to be found in the combined effects of the oxidation of zinc and its precipitation as hydroxide, carbonate, and complex ferrocyanide, the precipitation of lime as carbonate and the settling out of slimes. The electrical precipitation by local action having proved a failure, the author used an extraneous source of current and a special form of cell. Carbon anodes, either plain or coated with platinum sponge, had to be given up as they soon became disintegrated. Lead in an alkaline solution became coated with a non-adherent oxide and the peroxide of lead plates, as used in accumulators; he did not feel justified in using them on account of difficulty of handling and expense. They are, however, strongly recommended by Andreoli (*this Rev.*, 4, 78). A varnished lead plate finally proved satisfactory for the current of 0.4 amperes per square foot of anode area. The varnish consisted of 1 vol. linseed oil (boiled with litharge), 2 vols. Brunswick black (solution of asphaltum in turpentine) and one-third vol. graphite, and the whole diluted with turpentine to thin the mixture; two coats were required. As a diaphragm 14-oz. cotton duck made waterproof with either tannates or chromates of albumen or gelatine was very satisfactory. In order to make the solution passing by the anodes conductive, 0.02 per cent. carbonate of soda was added; the gold solution passing by the cathode was already a conductor. The cathode zinc shavings were held in cages of perforated sheet-zinc having a perforated central division wall and six trays of similar character, the whole being enclosed in a bag. The precipitating box had 90 compartments, 50 narrow

(4-inch) and canvas-framed for the anodes and 40 wide (13-inch) for the cathode cages. At the head of the box the solution, made alkaline with sodium carbonate, flowed into the anode divisions, the gold solution into the cathode divisions. The current averaged 200 amperes and 6 volts. It is expected that the resistance in future plants may be overcome by 3 volts. The precipitation was satisfactory throughout; the clean-up was made by treatment with sulphuric acid, followed by fusion with alkali fluxes. The author believes that his process will give at least 6 dwts. more profit per ton of slimes than any other.

A Blast-furnace Problem with Zinc. By W. W. Taylor. *Eng. Min. J.*, 67, 469.—The iron ores smelted in western Virginia containing about 0.1 per cent. zinc form hard cadmias at the throat of the furnace and dusty oxides in the stoves, flues, etc. A hard, strong cadmia had the following composition: Zn, 73.00; SiO_2, 2.50; FeO and Al_2O_3, 3.00. With slow driving and a large percentage of fuel, little trouble occurs from the presence of zinc; with hard driving and a low consumption of fuel the zinc accretions near the throat of the furnace have to be removed every few months. It has been found that the cadmias collect especially opposite the down-take; in order to prevent their forming large accretions which greatly disturb the running of the furnace and render their handling difficult when broken off, the gases are drawn off by four flues. The cadmias fill the intervening spaces, their weights rarely exceeding 12 tons.

The Whiting Process for Making Portland Cement. By C. Kirckhoff. *Iron Age*, 63 (No. 10), 9.—The process aims to make Portland cement from the iron blast-furnace slag of the Illinois Steel Co. A plant producing 500 barrels a day having proved successful at the "North Works," another with a daily capacity of 1500–2000 barrels for the "South Works" is being erected. The liquid slag running from a trough is granulated by a stream of water issuing from a nozzle under a pressure of 80 lbs. to the square inch; it is then conveyed to a rotary dryer, thence to Griffin pulverizers, and lastly the dry pulp to Davidson tube-mills. A tube-mill consists of a horizontal cylinder, 4 feet in diameter and 16 feet long and lined with porcelain, making about 27 revolutions per minute. It is filled to half its volume with flint pebbles, 1–2 inches in diameter, which grind up and mix intimately the pulverized slag, burnt lime and other ingredients making up the charge. This is fed through the trunnion at the upper end and discharged at the periphery at the lower end. At least 95 per cent. of the mixture, the finished cement, will pass a screen with 40,000 meshes to the square inch.

Cast Iron. By R. G. G. Moldenke. *The Foundry*, 13, 222-231 ; 14, 14–16.—The paper gives a general review of the different pig irons used in casting, of the cupola and reverberatory methods of melting, and of the physical and chemical properties of cast iron. Cast iron is defined as an iron carrying over 1½ per cent. silicon, which, after casting, is not subjected to further heat treatment.

The Melting-point of Cast Iron. By R. Moldenke. *J. Am. Foundrymen's Assoc.*, 5, 282–292.—On account of the difficulty of judging the temperatures of melted irons of different chemical compositions by the eye alone (*e. g.*, a ladleful of one iron, appearing as hot as melted steel while in reality it is cooler than one which seems to be dull-red), induced the author to determine the melting temperatures experimentally. He used the LeChatelier pyrometer, modifying it by covering the exposed couple with a fire-clay tip. This can be attached to the iron pipe holding the platinum and platinum-rhodium wires, insulated in this case with asbestos. Using the tip, a correct reading is obtained in 1¾ minutes, when the couple is plunged cold into the liquid metal ; if it is first brought to a red-heat this can be done in a few seconds. The melting-points of 73 samples of analyzed pig iron, ferro silicon, silico-spiegel, cast iron, and alloys of steel were determined and tabulated by the author.

Method of Casting Test-bars for the American Foundry Association Testing Committee. By T. D. West. *J. Am. Foundrymen's Assoc.*, 5, 301–305.

The Yard-Grading of Pig Iron. By W. B. Phillips. *J. Am. Foundrymen's Assoc.*, 6, 6–17.—In grading pig iron for foundry purposes according to the appearance of the fracture there are distinguished at present the following 13 classes: Open and close silver-gray irons show a fine silvery luster on a fresh surface, are flaky, have little or no granulation, are weak, and contain 5–6 per cent. silicon. Nos. 1 and 2 soft irons begin to show granulation, have light color, a smooth surface, and a weak fraction, the Si ranges from 3–4 per cent., they are less flaky than silvery irons, less jagged than foundry irons, and darker than silvery irons on account of the graphite they contain. No. 1 foundry is dark, has a granulation that is very open and regular, its crystallization is well marked, and the face is rough to the feel, the Si runs from 2.50–3.00 per cent. No. 2 foundry has the same general character as No. 1, it is closer grained, shows a finer crystallization, and while the color may be the same as in No. 1 it lacks the blackish-gray velvety quality, the Si runs from 2.25–2.50 per cent. ; No. 3 foundry with

2.00–2.25 per cent. and No. 4 foundry with 1.75–2.00 per cent. silicon form the transition to gray forge with 1.50–1.75 per cent. This has a pebbled granulation in the center with mottled edges, the face is blistered, pitted and often honeycombed. Mottled iron with 1.25–1.50 per cent. silicon has next to no granulation, but shows a pepper-and-salt appearance on a fresh fracture. Finally, white iron has no granulation whatever, is white but not silvery, the silicon runs from 0.1–0.6 per cent. The author shows how unsatisfactory is the present method of grading, when *e. g.* silvery irons are hardly produced at all and the silicon irons, which formerly analyzed 3–5 per cent., now carry 2–3 per cent. silicon without having changed their appearance correspondingly so as to allow a satisfactory grading by fracture. Grading alone by the silicon content is simple, but unsatisfactory ; to it ought to be added a ratio between silicon and combined carbon for soft and foundry irons and the percentage of sulphur as affecting gray forge, mottled, and white irons. This brings the grading nearly to a chemical basis. The use to which a particular pig iron is to be put is indicated by its chemical composition and not by its color, fracture, granulation of fracture, etc. In large works which have uniform ore charges, the outer appearance may serve as a guide, if it is continually checked by work in the chemical laboratory. Retaining the old nomenclature, the author proposes the following six grades, with the understanding that in special cases the percentage of phosphorus be also included :

Kind of iron.	Si.	Comb. C.	S.
Silvery	5–6	0.10–0.30	0.01–0.04
Soft	3–5	0.20–0.60	0.01–0.05
Foundry	2–3	0.30–0.90	0.01–0.07
Gray Forge	1–2	0.40–1.25	0.04–0.09
Mottled	0.6–1	0.50–1.80	0.06–0.11
White	0.1–0.6	1.00–2.50	0.08–0.30

On the Influence of Silicon upon the Heat of Solution of Coke Cast Irons. By E. D. Campbell and W. E. Hartman. *J. Am. Chem. Soc.*, 20, 690–695.—The metallurgical interest of this paper lies in the question as to whether the form of silicon in which it is present in No. 1 foundry iron changes when with increase of temperature a blast-furnace produces lighter and lighter irons until silvery or glazed iron is made, which shows such different physical and chemical properties from No. 1 foundry. The conclusions arrived at are that in dissolving iron with 0.1–0.4 per cent. silicon and the carbon nearly all present in the graphitic form, the heat evolved by the oxidation of the silicon is proportional to the amount of silicon present. With low-silicon iron in which the carbon is largely present in the combined state, the heat made sensible by solu-

tion is much diminished owing to the heat consumed in decomposing iron-carbon compounds and possibly some compounds of iron, silicon, and carbon, or of carbon and silicon. Since the oxidation of 1 gram silicon evolves 3824 calories, and the maximum of calories evolved in dissolving cast irons in the experiments was 3303 calories, it is evident that the decomposition of the compounds of silicon with iron must consume a large amount of heat. Lastly, ferrosilicon, in which the percentage of silicon is nearly sufficient to correspond to the formula $SiFe_3$ is not decomposed by ammonium copper chloride.

The Allotropic Theory and the Hardening Power of Low-Carbon Steel. By H. M. Howe. *The Metallographist*, 2, 77–78.—An answer to Ledebur's discussion of the author's experiments on the hardening of low-carbon steel.

[Contribution from the Massachusetts Institute of Technology.]

REVIEW OF AMERICAN CHEMICAL RESEARCH.

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Arthur A. Noyes, Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby and M. L. Fuller; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

ANALYTICAL CHEMISTRY.

ULTIMATE ANALYSIS.

W. H. Walker, Reviewer.

The Volatilization of the Iron Chlorides in Analysis and the Separation of the Oxides of Iron and Aluminum. By F. A. Gooch and Frank S. Havens. *Am. J. Sci.*, 157, 370–374.—When ferric oxide is submitted to the action of dry hydrochloric acid gas at a temperature of 180°–200°, it volatilizes partially as ferric chloride, but leaves ultimately a crystalline residue of ferrous chloride not volatilized at even 500°. If, however, the oxide be first heated to 450°–500° before the brisk stream of hydrochloric acid gas begins to act, or if the acid contains a little chlorine when it is passed over at 200°, the entire mass of oxide is converted and volatilized without residue. Results of experiments to apply this principle to the separation of the mixed oxides of iron and aluminum are perfectly satisfactory, showing that the separation of the iron oxide is complete at 450°, when the mixed oxides are submitted at once to the action of the gas, or at 200°, when chlorine is mixed with the acid gas.

The Use of Compressed Oxygen in Elementary Organic Analysis and of Soda-lime in the Quantitative Determination of Carbon Dioxide. By Francis G. Benedict and Olin F. Tower. *J. Am. Chem. Soc.*, 21, 389–398.—Inasmuch as oxygen stored under pressure in steel cylinders was found to contain less moisture and carbon dioxide than that made in the ordinary way and used from a gasometer, the author considers the use of the compressed gas an advantage in elementary or-

ganic analysis, and describes a piece of apparatus by the use of which the pressure of the gas may be controlled. Freshly prepared soda-lime was found to lose less moisture during absorption of carbon dioxide than potash bulbs.

Determination of Calcium and Magnesium in Ashes. By J. K. Haywood. *J. Am. Chem. Soc.*, 21, 508–511.—Instead of filtering off the basic acetate precipitate containing the iron and phosphoric acid and washing it free from the filtrate in which calcium and magnesium are to be determined, the author finds it sufficiently accurate to filter only an aliquot part of the supernatant liquid and to precipitate the calcium and magnesium from this. Analytical data are given to show the accuracy of the process.

Tests for Boric Acid. By Victor Lenher and J. S. C. Wells. *J. Am. Chem. Soc.*, 21, 417–420.—An experiment described by Newth in his "Chemical Lecture Experiments" for the production of boric ether is applied as a qualitative test for boric acid. It is found more delicate than the usual method of sulphuric acid and alcohol in an evaporating dish. It is carried out as follows: In a test-tube fitted with a cork, through which passes a glass tube drawn out to a jet, are placed the borate, sulphuric acid, and alcohol. The boric ether formed when the mixture is heated burns at the jet with the characteristic flame, copper and barium not interfering with the test. Comparative tests of all the ordinary methods, however, show turmeric paper to be the most sensitive.

The Constitution of the Ammonium Magnesium Phosphate of Analysis. By F. A. Gooch and Martha Austin. *Am. J. Sci.*, 157, 187–198.—The results of this extended investigation show that in determining magnesium by the procedure in ordinary use, the tendency is strong towards too high results, and it is made evident that the error is due to the combined effect of excesses of the precipitant, the ammonium salt, and free ammonia in throwing down a compound of phosphoric acid richer in ammonia and poorer in magnesium than the normal salt, NH_4MgPO_4. This tendency is counteracted, and the consequent error entirely eliminated, by pouring off the supernatant liquid (through the filter subsequently to be used to collect the precipitate) as soon as the precipitate subsides, dissolving the phosphate in the least amount of hydrochloric acid, and after dilution reprecipitating by a faint excess of ammonia. This procedure precipitates the normal salt, which should be washed with faintly ammoniacal water. In the precipitation of a soluble phosphate by magnesium mixture the results are much the same, and the use of strong ammonia (1 : 3) is again shown to

be not only unnecessary but disadvantageous. Good results may be expected when the solution of the phosphate containing a moderate excess of a magnesium salt and not more than ten per cent. of ammonium chloride is precipitated by making slightly alkaline, and then washed with slightly alkaline wash-water.

A Modification of Pierce's Method for the Determination of Arsenic in Ores. By J. F. Bennett, Jr. *J. Am. Chem. Soc.*, 21, 431–435.—The modifications consist essentially in substituting acetic acid for a mineral acid when neutralizing the solution of the alkaline fusion, and using phenolphthalein as indicator instead of litmus. The details of the improved method are given in full, and to these are added many analytical data.

The Influence of Hydrochloric Acid in Titration by Sodium Thiosulphate, with Special Reference to the Estimation of Selenious Acid. By John T. Norton, Jr. *Am. J. Sci.*, 157, 287–293.—In the iodometric method for the determination of selenious acid of Norris and Fay (*this Rev.*, 4, 31) it was found that the presence of hydrochloric acid did not influence the results providing the reaction took place at the temperature of melting ice. By titrating decinormal solutions of sodium thiosulphate and iodine in the presence of hydrochloric acid under varying conditions of temperature, concentration of acid, and excess of thiosulphate present, the author finds that without certain precautions the presence of hydrochloric acid influences the results very considerably. If the excess of thiosulphate be not more than 20 cc., however, and the concentration of acid be not greater than 10 cc. of hydrochloric acid (sp. gr. 1.12) in 400 cc. of solution, the above process is shown to be very accurate.

The Titration of Oxalic Acid by Potassium Permanganate in the Presence of Hydrochloric Acid. By F. A. Gooch and C. A. Peters. *Am. J. Sci.*, 157, 461–467.—Although it has been stated by several investigators that hydrochloric acid does not interfere with the titration of oxalic acid by potassium permanganate, the authors give experimental data which go to show that the error introduced by the presence of hydrochloric acid is very appreciable. As is the case with the oxidation of ferrous chloride, however, the presence of a suitable amount of a manganous salt entirely prevents the action of the permanganate on the acid.

On the Determination of Sulphur in Sulphites. By A. Bourgougnon. *J. Am. Chem. Soc.*, 21, 469–470.—The sulphite in dilute hydrochloric acid solution is treated with a solution of hydrogen peroxide, and the sulphuric acid formed is precipitated and weighed as barium sulphate.

PROXIMATE ANALYSIS.

W. H. WALKER, REVIEWER.

Estimation of the Lime, Potash, and Phosphoric Acid in Hawaiian Soils Probably Available for the Immediate Crop. BY WALTER MAXWELL. *J. Am. Chem. Soc.*, 21, 415–417.—In order that the lime, potash, phosphoric acid, and other bases may be dissolved from the soil in the proportion that they are removed by "cropping," the sample is treated with a one per cent. solution of aspartic acid for twenty-four hours. This solution is then evaporated, and the residue is ignited and analyzed by the usual methods.

Notes on the Analysis of Dynamite and Gelatine-Dynamite. BY F. W. SMITH. *J. Am. Chem. Soc.*, 21, 425–431.—Procedures for the analysis of explosives containing nitroglycerine are given in detail, together with the results of several analyses which may be considered typical of this class of products.

ASSAYING.

H. O. HOFMAN, REVIEWER.

The Assay of Telluride Ores. BY C. H. FULTON. *School Mines Quart.*, 19, 419–426.—This paper gives the results of crucible and scorification assays made on two Cripple Creek gold ores assaying about 5 and 450 oz. gold per ton. They show that the crucible assay is to be preferred by far to the scorification method; that in the crucible assay an excess of litharge has a beneficial effect; that the lead-buttons weighing 20–28 grams must be malleable so as to permit direct cupelling and not necessitate any scorification, which is connected with large losses; that the slags carry off considerable gold and have to be reassayed; and that the absorption by the cupel need not be taken into account.

GEOLOGICAL AND MINERALOGICAL CHEMISTRY.

W. O. CROSBY, REVIEWER.

The Petrographical Province of Essex County, Mass. BY HENRY S. WASHINGTON. *J. Geol.*, 6, 787–808; 7, 53–64, 105–121, 284–294.—Although Essex county is a region of great petrographic diversity and interest, and its rocks have received much attention from geologists in the past, and are the subject of a considerable literature, this series of papers is the first systematic and comprehensive petrological study of this now classic area. The author confines his attention to the igneous rocks, which include chiefly granites, quartz-syenites, syenites, nephe-

line-syenites, essexites, diorites, and gabbros, cut by numerous dikes and with later flows of rhyolite. The entire series is regarded as pre-Carboniferous and post-Cambrian, having cut and metamorphosed the Cambrian strata of the region. The descriptions are supplemented by chemical analyses and a general discussion of the results, including a comparison of this region with others of similar character. The *granites* are all hornblendic, but contain also more or less glaucophane and biotite, and the accessories include danalite, fayalite, allanite, epidote, zircon, magnetite, apatite, fluorite. The feldspar is all of the most acid alkali varieties, including orthoclase, microcline, and albite, occurring largely as highly typical microperthites and cryptoperthites. The analysis shows a typical acid granite, rich in potash and low in lime and iron oxides. The mineralogical composition, as for most of the rocks studied, is calculated from the analysis. Included masses of darker color and finer grain are found to consist of the same essential minerals as the granite, but in different proportions, analysis showing 10 per cent. less silica and much more iron oxide, corresponding to a *quartz-syenite*. *Akerite*, or *augitic quartz-syenite* is found to be almost as abundant as the granites, and the analysis shows it to be closely similar in composition to the dark inclusions of the granite, and like these it is regarded as a differentiation of the granite magma. Another very slight differentiation is afforded by the *nordmarkite* or *mica-hornblende-quartz-syenite*, and the more acid character of this type finds mineralogical expression in the substitution of biotite and hornblende for augite. More strongly contrasted with these, and with an unquestionable claim to separate recognition is the *nepheline syenite*, which has, in comparison, a rather limited development. Two main structure types are recognized, a granitic and a trachytic, which shade into each other and correspond to the *ditroite* and *foyaite* of Brögger, the latter predominating. An analysis is given for each type, the only notable difference being that the foyaite is rather richer in soda and poorer in iron oxide than the ditroite, while both are notably poorer in lime and magnesia than the nepheline syenites of other regions, and higher in silica than the average, agreeing closely with the albite-rich litchfieldite of Bayley. Next comes, as a facies of the nepheline syenite, and showing the same structural distinction, the nepheline-poor to nepheline-free rock known as *pulaskitic syenite* or *pulaskite*. An analysis of each phase of this rock shows that it is decidedly more acid than the normal type of nepheline syenite. This series closes with the *orbicular syenite*, which occurs as rounded inclusions in granite and owes its name to the fact that each prominent phenocryst of hornblende is surrounded by a narrow zone of white feldspar. *Essexite*, described as essentially a basic monzonitic rock con-

taining both lime-soda and alkali feldspars and feldspathoids, is confined to the immediate vicinity of Salem Neck. It is quite distinct from the nepheline syenites, by which it is cut, but grades into the diorites. Sears regards it as the earliest crystallized and most basic portion of the nepheline-syenite magma. Several structural and mineralogical varieties are recognized, and an analysis of a specimen selected by Sears as representing the type shows a decidedly basic rock (SiO_2, 46.99) rich in lime and soda. *Diorite* has a large development in Essex County. It is highly varied and represents transitions from the essexites to the akerites. The analysis shows a rather basic rock for a diorite (SiO_2, 51.82), but, on the other hand, both the silica and alkalies are too high for a gabbro. Besides the main type of diorite, which is often more or less quartzose, the author describes a *quartz-augite-diorite* and a *porphyritic diorite*, with an analysis of the latter. The *gabbro* of Nahant is next described, and the analysis shows that it is low in silica (43.73) and rich in lime (10.99) as a gabbro should be, but also rather poor in magnesia, high in titanium oxide and alumina, and rather high in alkalies, for a gabbro. The hyperitic essexite of Rosenbusch, called also hyperitic diorite in one of the earlier papers of this series, is shown by a later analysis to be more properly a *hornblende-gabbro* (SiO_2, 45.32). The dike rocks next receive attention, beginning with the granitic dikes. These include *aplite*, the very narrow dikes of which are wholly confined to the granite, with which they are found to agree closely in composition, and *quartz-syenite-porphyry*, which is found to be essentially identical in composition with the nordmarkite. The rocks of the *paisanite-sölosbergite-tingnaite* series all form dikes, although of *paisanite* but a single dike has been observed, the analysis of which is almost identical with the aplite. The *sölosbergite* forms numerous dikes, which are described in detail, with two original analyses and one quoted from Rosenbusch. Three *tingnaite* dikes are described, with two analyses, the more basic analysis representing an *analcite tingnaite*. The basic dikes include dikes of *camptonite* (one analysis), *vogesite*, very numerous dikes of *diabase* (one analysis), and dikes of *labradorite porphyry* or *porphyritic diabase*. The work closes with a brief account of the extensive rocks, including the *rhyolite* and *keratophyre* of Marblehead Neck, and with an analysis of each.

M. L. Fuller, Reviewer.

Augite-Syenite Gneiss near Loon Lake, New York. By H. P. Cushing. *Bull. Geol. Soc. Am.*, 10, 177–192.—This is a greenish-gray, massive, igneous rock of cataclastic structure and medium grain, which resembles some phases of the Anorthosites of the region, and was formerly classed with them. It cuts and encloses gneissic rocks which are regarded as unquestionably

sedimentary and referred to the Greenville series, and is, in turn, cut by the diabases, the youngest of the pre-Potsdam rocks. The syenite is essentially composed of microperthite, augite, and hypersthene, with quartz always present in varying and commonly slight amount. Other component minerals include zircon, apatite, magnetite, garnet, hornblende, oligoclase, and sometimes biotite, titanite, allanite, and pyrite. The analysis, by E. W. Morley, gives: SiO_2, 63.45; TiO_2, 0.07; Al_2O_3, 18.31; Fe_2O_3, 0.42; FeO, 3.56; MnO, none; CaO, 2.93; BaO, 0.13; MgO, 0.35; K_2O, 5.15; Na_2O, 5.06; P_2O_5, trace; loss, 0.30; total, 99.73. Assuming the augite to be a calcium, ferrous-iron, aluminum silicate, the author calculates from the analysis the proportions of the chief component minerals as follows: Magnetite, 0.73; orthoclase, 30.39; albite, 42.70; anorthite, 4.51; hypersthene, 2.03; augite, 12.02; quartz, 7.07. This result agrees well with that obtained by separation with heavy solutions. The plagioclase is a nearly pure albite, $Ab_{19}An_2$, and the microperthite is approximately Or_3Ab_5. Six other analyses are quoted for comparison, and the Loon Lake rock is seen to agree very closely with several other syenites, and especially with those of Diana, N. Y., Mt. Ascutney, and Gloucester, Mass., which are all referred to an acid phase of the variety called akerite by Brögger. Other Adirondack localities are briefly described, and the rock is shown to vary within quite wide limits, varying from a granite to a syenite more basic than the one analyzed. The relations of the syenites to the anorthosites are also discussed, the conclusion being that the syenites are probably a result of differentiation in the anorthosite magma after reaching its place of final cooling, and in part are somewhat later in date.

Origin of Grahamite. By I. C. White. *Bull. Geol. Soc. Am.*, 10, 277–284.—The grahamite of Ritchie County, West Virginia, first described by Lesley in 1863, and more fully by Fontaine in 1873, fills a vertical fissure about two-thirds of a mile long, varying in width from a few inches at the ends to 4 and 5 feet in the middle. The fissure is at right angles to and undoubtedly genetically connected with the Burning Springs-Eureka anticlinal which, with dips of from 30° to 70°, crosses the formation about 7 miles west of the deposit. Lesley predicted that "this gash was once an open fissure communicating with some reservoir of coal oil (petroleum) which still, it may be, lies beneath it undisturbed." Oil wells drilled during the past decade have fully verified this prediction, developing at a depth of 1500 to 1600 feet and in close proximity to the grahamite fissure, a pool of oil which is but part of the prolific Cairo oil field. Hence the author concludes that there can be no doubt

whatever that the fissure made by tension from the Burning Springs-Eureka uplift was filled with petroleum from this pool, and that subsequently the oil was gradually converted by oxidation from infiltrating water into grahamite without any heat other than that afforded by the normal temperature of the earth. In this connection he cites Jeaney's experimental production of grahamite by passing heated air through petroleum for several hours. As a corollary from this conclusion, albertite, gilsonite, uintaite, and practically all forms of asphalt, including, as suggested by Diller, the "pitch" coal of Coos Bay, Oregon, are oxidized petroleum, and the wonderful deposit of asphalt on the island of Trinidad is regarded as an old oil pool uncovered by erosion and hardened by volatilization and oxidation.

A Contribution to the Study of Contact Metamorphism. By J. Morgan Clements. *Am. J. Sci.*, 157, 81–91.—This paper is essentially a detailed account of a somewhat normal instance of contact metamorphism not hitherto described. It occurs in the Lower Huronian iron-bearing formation of the Crystal Falls district of the upper peninsula of Michigan, where the Mansfield slate formation of the Michiganie Valley is cut by large and continuous masses of coarse dolenite (diabase). The intrusions show no evidence of endomorphic action and are not described; but the slate, which is an undoubted sedimentary deposit, exhibits, as we approach the igneous contact, increasing metamorphism, and the successive phases known as phyllites, tpilosites, desmosites, and adinoles are observed in normal order. The least altered rocks, the normal clay slates, are found on microscopic examination to be of a semicrystalline character, containing, besides elastic quartz and original interstitial matter, secondary white mica, rutile, hematite, and actinolite. The phyllites are similar, except that they are more lustrous, and the interstitial material has been changed to white mica. The spilosites, desmosites, and adinoles are the true contact products. They are dense, flinty, "hornestone-like" rocks, which show in some cases the fine banding of the original slates, while others are very characteristically spotted. The mineralogical components are quartz, feldspar (albite), biotite, chlorite, white mica, actinolite, rutile, epidote, and iron oxide. In the first two varieties chlorite is the chief dark constituent with little or no actinolite, while the opposite relation holds for the adinoles. Complete analyses by George Steiger and H. N. Stokes are given for the normal clay slates, spilosites, and adinoles. A comparison of the analyses shows a marked increase of silica as the dolerite is approached, and a corresponding diminution of alumina and iron as well as of water and carbonaceous matter. The most noteworthy contrast between the clay slate and the

contact rocks is shown in the relations of potash and soda. For the clay slate the percentages are 5.73 and 0.54, respectively, while in the contact rocks these proportions are reversed, the successive values for potash being 0.70, 0.22, 0.15, and for soda 6.72, 8.22, 6.57. This agrees with the fact that, while albite is wanting in the clay slate, it is an abundant constituent of the contact rocks. The author concludes that the changes in ultimate chemical composition are probably best explained as due to an actual transfer of material, possibly in the form of a soda silicate, from the basic igneous rock to the intruded slate.

A Contribution to the Geology of the Pre-Cambrian Igneous Rocks of the Fox River Valley, Wisconsin. By SAMUEL WEIDMAN. *Wis. Geol. and Nat. Hist. Survey, Bull. No.* 3, *Science Series No.* 2, 1–63.—The areas of igneous rocks described in this paper are a part of the cordon of hills and ridges of pre-Cambrian rocks that lie outside the more continuous crystalline cove of central and northern Wisconsin. These outlying hills were islands in the early Paleozoic seas, and around them are deposited the later horizontal formations of sandstone and limestone. Among the pre-Cambrian outliers are to be found rocks of both sedimentary and igneous origin; but those of the Fox River district are wholly igneous, of both plutonic and volcanic nature. Three types are described in great detail, *viz.*, the Utley metarhyolite, Berlin rhyolite-gneiss, and Wanshara granite. They are regarded as of Keweenawan age, and the close agreement of the bulk analyses shows that they are essentially consanguineous and belong with the Baraboo rhyolite to a petrographic province of considerable extent. The acid character of these rocks limits the mineral composition chiefly to quartz and feldspar. An analysis of the feldspar phenocrysts of the Utley metarhyolite shows that they are a soda-lime feldspar with a considerable amount of potash; and in harmony with this composition, the microscope reveals in most cases a micropesthitic structure. This is discussed at some length and shown to be partly original and partly secondary; and the latter is believed to be due in part to an enlargement or outgrowth of the original plagioclase phenocrysts, and in part to intergrowths or regeneration of older plagioclase, the latter process being regarded as allied to paramorphism and not unlike the process of schillerization as described by Judd.

On Hardystonite, a New Calcium Zinc Silicate from Franklin Furnace, New Jersey. By JOHN E. WOLFF. *Proc. Am. Acad.*, 34, 479-481.—This is a granular, white, vitreous mineral which is intimately associated with the willemite, rhodonite, and franklinite of the zinc mines. The crystallization

is tetragonal with a good basal cleavage and secondary cleavages parallel to the prisms of the first and second orders. The specific gravity is 3.95, and hardness between 3 and 4. The analyses, recalculated to 100 and omitting iron and ignition as non-essential, give as the normal composition: SiO_2, 38.34; ZnO, 24.45; MnO, 1.50; CaO, 34.07; MgO, 1.62. The molecular ratios give (ZnMn)O : (CaMg)O : SiO_2 as 1 : 2 : 2, with Mn to Zn and Mg to Ca as 1 to 15; and the formula is hence (ZnMn)O,2(CaMg)O,2SiO_2 or ZnO,2CaO,2SiO_2, the theoretical composition of the latter being: SiO_2, 38.34; ZnO, 25.88; CaO, 35.78.

[Contribution from the Massachusetts Institute of Technology.]

REVIEW OF AMERICAN CHEMICAL RESEARCH.

Vol. V. No. 10.

Arthur A. Noyes, Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby and M. L. Fuller; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

GENERAL AND PHYSICAL CHEMISTRY.

A. A. Noyes, Reviewer.

The Theory of the Formation of Nickel Sulphide. By J. Livingston R. Morgan, and A. H. Gotthelf. *J. Am. Chem. Soc.*, 21, 494–502.—The authors attempt to show that the well-known fact that nickel and cobalt sulphides when once formed are not dissolved by acids of a concentration much greater than is required for preventing entirely their precipitation by hydrogen sulphide, can be explained simply by an application of the principles of mass-action and of electrolytic dissociation, assuming an appropriate value for the solubility of the sulphides. The considerations of the authors are, in the reviewer's opinion, erroneous in some essential points (thus this is true of the statements that no undissociated nickel sulphide or hydrogen sulphide will be formed till the product of the concentrations of their respective ions reaches the value of the "solubility-product"), but it is unnecessary to discuss these in detail, since it is *a priori* evident that the principles of equilibrium as ordinarily applied cannot possibly explain the phenomenon in question; for, if equilibrium exist between the four substances, $NiCl_2$, H_2S, HCl, and NiS (solid), when the first two are present in large amount and the last two in very small amount, it is clear that the conditions must be *far* removed from those of equilibrium when the last two compounds are alone brought together, and conversely. The probable explanation, previously suggested by Ostwald (*Scientific Foundations of Analytical Chemistry*, p. 149), of this apparent anomaly, is that after precipitation the nickel sulphide rapidly undergoes a change in its chemical nature (perhaps a dehydration), the new form being

much less soluble in water and therefore in acids than the original one. By quantitative experiments Ostwald has proved that this is the case with zinc sulphide, and the same property, in a much more pronounced degree, seems to be possessed by nickel and cobalt sulphides.

The Effect of Diionic Electrolytes on the Solubility of Triionic Electrolytes with Different Ions. By Arthur A. Noyes and Edward S. Chapin. *J. Am. Chem. Soc.*, 21, 511–516.—The authors derive the theory of the phenomenon mentioned in the title and communicate experiments confirming it on the solubility of calcium hydroxide in water and ammonium chloride solutions.

The Theory of the Separation of Barium, Strontium, and Calcium from the Mixed Sulphates. By J. Livingston R. Morgan. *J. Am. Chem. Soc.*, 21, 522–526.—It is shown that the separation of the sulphates named, by ammonium carbonate or a mixture of potassium sulphate and carbonate, is readily explained by the dissociation theory and the laws of solubility-effect.

The Atomic Mass of Tungsten and the Preparation of Sodium Pertungstate by Means of the Electric Current. By George Edward Thomas. *J. Am. Chem. Soc.*, 21, 373–381.—In the first part of the article it is shown that two samples of tungsten trioxide, prepared from distinct minerals, scheelite and wolframite, are apparently identical, but that both of them fail to give concordant values of the atomic weight when reduced to the metal or when the latter is reoxidized ; also that the method of determining the atomic weight from the loss of weight occurring when crystallized sodium tungstate is heated sufficiently to expel the water is an unsuitable one. In the second part the author describes the results of electrolyzing sodium tungstate, considering that a pertungstate is formed thereby, since a substance liberating chlorine, iodine, and ozone was obtained, though not in a state of even approximate purity.

The Surface-Tensions of Aqueous Solutions of Alkaline Chlorides. By C. E. Linebarger. *J. Am. Chem. Soc.*, 21, 411–415.—Equimolecular solutions of potassium, sodium, and lithium chlorides are found to have the same surface-tension ; and their surface-tension is found to be only approximately a linear function of the concentration.

[Contribution from the Massachusetts Institute of Technology.[

REVIEW OF AMERICAN CHEMICAL RESEARCH.

Vol. V. No. 11.

Arthur A. Noyes, Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby and M. L. Fuller; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

ANALYTICAL CHEMISTRY.

ULTIMATE ANALYSIS.

H. P. Talbot, Reviewer.

Carbon Combustions in a Platinum Crucible. By P. W. Shimer. *J. Am. Chem. Soc.*, **21**, 557–568.—By means of an ingeniously-devised water-cooled stopper, an ordinary platinum crucible is made to take the place of the usual combustion tube, the combustion taking place in a current of air, and the heat being applied by means of a blast-lamp. The gases, on leaving the crucible, pass over a layer of heated cupric oxide, then over beads moistened with cold water, and finally through the usual absorption apparatus. The results obtained are highly satisfactory, and the time required for the completion of the combustion is small. The original article furnishes details of construction and use which are of unusual interest, and suggest that the apparatus may find other uses beside that in the determination of carbon.

The Determination of Carbon and Hydrogen in Organic Substances Containing Nitrogen. By O. F. Tower. *J. Am. Chem. Soc.*, **21**, 596–605.—The author finds that during the combustion of amido compounds, such as urea, hippuric acid, and paratoluidine, no oxides of nitrogen are formed which are absorbed by concentrated sulphuric acid or soda-lime, even in the absence of a copper spiral. The same statement applies to the combustion of nitraniline and dinitrobenzene, but picric acid required the introduction of a copper spiral for the accurate determination of the carbon and hydrogen.

A Volumetric Method for Magnesium. By Richard K. Meade. *J. Am. Chem. Soc.*, 21, 746–752.—The magnesium is precipitated as magnesium ammonium arsenate, this precipitate dissolved in dilute hydrochloric acid, after which potassium iodide is added to the solution, and the liberated iodine is titrated with sodium thiosulphate solution. The results obtained are quite satisfactory.

The Estimation of Arsenic in Paris Green. By Thorn Smith. *J. Am. Chem. Soc.*, 21, 769–772.—The Paris green is treated with a solution of sodium hydroxide which, in the presence of the arsenite, causes a precipitation of cuprous oxide. This is removed by filtration, and, after acidifying with hydrochloric acid, potassium iodide is added, the liberated iodine is reduced by the cautious addition of sodium thiosulphate, and the arsenite is determined by titration with iodine. (Compare also the "*Volumetric Method for Magnesium*" *above*).

A New Method for the Direct Determination of Alumina in the Presence of Iron, Manganese, Calcium, and Magnesium. By William H. Hess and E. D. Campbell. *J. Am. Chem. Soc.*, 21, 776–780.—The solution of the chlorides of the metals is made nearly neutral with ammonia, ammonium bisulphite is added to reduce the iron, and then one or two cc. of phenylhydrazine. This precipitates the alumina and the phosphoric acid. The precipitate is washed with a solution of phenylhydrazine bisulphite, and then ignited. Chromium may be separated from iron in the same way.

The Determination of Antimony in Ores. By Thomas Brown, Jr. *J. Am. Chem. Soc.*, 21, 780–789.—The author gives a detailed account of methods of analysis applicable, in particular, to Mexican ores.

Electrolytic Determination of Zinc in the Presence of Manganese. By Emil J. Riederer. *J. Am. Chem. Soc.*, 21, 789–792.—The zinc is deposited on a silver-coated platinum dish, from solutions containing lactic acid, ammonium lactate, and ammonium sulphate, and the solution is stirred during the deposition, which requires from four to five and one-half hours for completion. The deposited zinc is free from manganese.

The Determination of Sulphur in Bitumens. By S. F. and H. E. Peckham. *J. Am. Chem. Soc.*, 21, 772–776.—The authors criticise statements made by E. H. Hodgson (see *this Rev.*, 5, 10) with respect to the accuracy of his method, and give in detail an account of the deflagration method as practiced by them.

W. H. WALKER, REVIEWER.

The Estimation of Iron in the Ferric State by Reduction with Sodium Thiosulphate and Titration with Iodine. BY JOHN T. NORTON, JR. *Am. J. Sci.*, **158**, 25–30.—Although a great deal of work has been done in the endeavor to estimate iron by reduction with sodium thiosulphate, no satisfactory method has as yet been proposed. The concentration of the ferric solution, the amount of acid present, the excess of thiosulphate used, and the length of time allowed for reduction, all greatly influence the reaction. After a great deal of experimenting the following conditions were found to give the most satisfactory results. The concentration of the iron solution must not be greater than 0.1 gram ferric oxide in 400 cc.; the amount of acid present should not exceed 1 cc. of the strong acid in the same volume; the time of reduction must be as short as possible to prevent progressive oxidation by air; and the excess of thiosulphate used should, for the same weight of iron, be not less than 15 cc. of a decinormal solution.

The Determination of Tellurous Acid in Presence of Haloid Salts. BY F. A. GOOCH AND C. A. PETERS. *Am. J. Sci.*, **158**, 122–126.—In a previous paper (*this Rev.*, **5**, 89) it was shown that the reaction between potassium permanganate and oxalic acid in acid solution is not influenced by the presence of chlorides, provided a quantity of manganous salt be added before titration. This modification is introduced into the method for determining tellurous acid by means of permanganate and oxalic acid. By causing the first oxidation to take place in alkaline solution, and making the final titration of the residual oxalic acid in acid solution in the presence of a manganous salt, the estimation of tellurous acid in the presence of chlorides and bromides was found quite satisfactory. In the case of an iodide, however, the presence of a manganous salt is not sufficient to prevent the action of the permanganate, and iodine is set free. As was shown by Norris and Fay (*this Rev.*, 4, 31), this free iodine may replace the oxalic acid as a measure of the excess of the permanganate used in oxidizing the tellurous acid, and its amount was determined by the authors by reducing it with standard arsenite solution in the presence of an excess of sodium bicarbonate.

An Iodometric Method for the Estimation of Boric Acid. BY LOUIS CLEVELAND JONES. *Am. J. Sci.*, **158**, 127–132.—In a volumetric method for the estimation of boric acid (*this Rev.*, 5, 52) it was found that the addition of mannite to the free boric acid made it possible to determine the acid by titration with standard alkali solution. If the solution is almost saturated

with mannite (glycerine does not serve the same purpose), the boric acid is rendered active enough to react with potassium iodide and potassium iodate setting free an amount of iodine equivalent to the metaboric acid present :

$$5KI + KIO_3 + 6HOBO = 3I_2 + 6KOBO + 3H_2O.$$

The iodine may be reduced with standard thiosulphate solution, and the amount of boric acid calculated. The necessary precautions as to concentration and temperature are given, and the results obtained seem very satisfactory.

The Double Ammonium Phosphates of Beryllium, Zinc, and Cadmium in Analysis. By Martha Austin. *Am. J. Sci.*, 158, 206–216.—The influence which varying conditions of temperature and concentration, excess of precipitant, and amounts of ammonium chloride have on the composition of the resulting insoluble phosphates thrown out of solution by means of sodium acid phosphate or microcosmic salt, has been studied with a view of determining the utility of the compounds in quantitative analysis. It was found impossible to precipitate beryllium as the true beryllium ammonium phosphate ; and no determinations made by weighing the pyrophosphate were sufficiently accurate to be of much value. In the presence of ammonium chloride (10 grams in 100 cc.), zinc ammonium phosphate may be obtained in the ideal condition, and forms the basis of a very accurate method for the determination of zinc. In the case of cadmium the precipitate with microcosmic salt in the presence of the same amount of ammonium chloride is also the true double ammonium phosphate, if it be allowed to stand for several hours before filtering. But there must, in this case, be no excess of ammonia, no free acid, and neither more nor less than the amount of ammonium chloride stated.

Separation of Iron from Chromium, Zirconium, and Beryllium, by the Action of Gaseous Hydrochloric Acid on the Oxides. By Franke Stuart Havens and Arthur Fitch Way. *Am. J. Sci.*, 158, 217–218.—The procedure for the separation of iron from chromium, beryllium, and zirconium is the same in the case of each metal, and analogous to that employed by the author (*this Rev.*, 5, 87) for the separation of iron from aluminum. The results given are very satisfactory.

Methods for the Iron Laboratory. By Frank L. Crobach. *Iron Trade Rev.*, 32, Nos. 24 to 29.—This paper consists of a series of five articles in which "the writer outlines for the benefit of beginners in foundry, steel works, and blast-furnace laboratories the methods he considers preferable."

PROXIMATE ANALYSIS.

A. G. WOODMAN, REVIEWER.

The Assay of Opium: A Supplementary Note. By H. M. GORDIN AND A. B. PRESCOTT. *Pharm. Rev.*, 17, 244–249.—The authors report an improvement in their process for the assay of opium (*Pharm. Arch.*, 1, 121; *this Rev.*, 4, 115), consisting in the use of a more desirable solvent for extracting the morphine and an adaptation to the use of standard acid for the volumetric estimation of the morphine.

The Distinction of True Extract of Vanilla from Liquid Preparations of Vanillin. By WILLIAM H. HESS. *Pharm. Rev.*, 17, 254–257.—The simplest means of proving the origin of vanilla extract consists in the separation and identification of the characteristic resin of which vanilla beans contain from four to eleven per cent. Simple tests for coloring-matters, chiefly caramel and certain azo dyes, and an examination of the behavior of the extract upon dilution with water are also found useful.

A New Test for Cocaine. By GEORGE L. SCHAEFER. *Am. J. Pharm.*, 71, 222–223.—In order to determine the freedom of commercial cocaine salts from other coca alkaloids, the author has devised a simple test based on the relative insolubility of the chromates of the coca alkaloids in dilute hydrochloric acid.

Assay of Nux Vomica. By W. O. RICHTMANN. *Pharm. Rev.*, 17, 208–210.—Attention is called to the necessity of using a greater quantity of decinormal sulphuric acid in testing the evaporated percolate obtained in making fluid extract of nux vomica.

A Contribution to the Chemistry of Butter-fat. By C. A. BROWNE, JR. *J. Am. Chem. Soc.*, 21, 612–633.—The author has determined in a number of samples of butter-fat the various physical and chemical constants that are usually determined in the examination of the fat together with a number of those not commonly found. Several of the methods and modifications employed are described in considerable detail.

The Assay of Belladonna Leaves. By FRANK X. MOERK. *Am. J. Pharm.*, 71, 320–326.—The author has shortened the time required for the assay of belladonna leaves by using a mixture of 90 parts, by weight, of 95 per cent. alcohol and 10 parts, by weight, of 10 per cent. aqua ammonia for extraction purposes instead of the menstruum usually employed (2 volumes alcohol and 1 volume water).

On Acetic Acid as a Substitute for Ethyl Alcohol in Extracting the Active Principles of some Officinal Drugs. By Edward R. Squibb. *Am. J. Pharm.*, 71, 305–320.—In continuation of his previous work upon this subject, the author has carried out experiments with cinchona, and finds that this drug is readily and completely exhausted, even when in fairly coarse powder, by ten per cent. acetic acid. A detailed procedure for the assay of cinchona is worked out and a description is given of a modified form of siphon extractor which has been found to work successfully.

Newer Observations Concerning the Detection of Blood by Means of the Guaiacum Reaction. By Edward Schaer. *Am. J. Pharm.*, 71, 361–370.—In a previous paper the author has proposed to improve the guaiacum-blood reaction, as ordinarily used, by substituting for the usual alcoholic guaiacum solution a five per cent. alcoholic solution of guaiacum resin. The intimate mixture of the coloring-matter of blood and guaiacum resin thus obtained may be preserved for an indefinite time and can at any time be used to exhibit the "guaiacum blue" with hydrogen peroxide or Hünefeld's reagent. A further improvement is now suggested consisting in the use of a solution of chloral hydrate to extract the blood stains. The stains, after being moistened with acetic acid, can be extracted either with a 70 per cent. chloral hydrate solution or with a one per cent. solution of guaiacum in aqueous chloral hydrate containing 70–75 per cent. of the latter. To the blood-guaiacum solution in aqueous chloral hydrate thus obtained is added either hydrogen peroxide solution or Hünefeld's liquid so that the two layers do not mix. The blue zone will appear at the place of contact. The guaiacum-blood test with chloral hydrate can also be applied to the identification of the hemin crystals of blood, which is often of great importance. A solution of guaiaconic acid in chloral solution can be substituted for the ordinary guaiacum solution if desired.

On the Determination of Added Water in Milk. By A. G. Woodman. *J. Am. Chem. Soc.*, 21, 503–508.—The most successful of the methods for the direct determination of the added water in milk is that based upon the specific gravity of milk from which the casein has been removed. The conditions necessary to obtain concordant results have been studied and tables are given showing the specific gravity of the serum from milks of varying dilution.

Paraffin as an Adulterant of Oleomargarine. By Joseph F. Geisler. *J. Am. Chem. Soc.*, 21, 605-608.—The amount of paraffin which has been found in oleomargarine varies from 5 to

11.76 per cent. Its presence is clearly indicated by the low specific gravity of the fat. If the amount present is over three per cent. it will separate out when the alcoholic soap solution obtained by the Reichert method is diluted with an equal volume of water. The appearance of the fat under polarized light is shown by photomicrographs.

An Examination of Commercial Flour. By HENRY KRAEMER. *J. Am. Chem. Soc.*, 21, 650–663.—The author proposes a microchemical method for the estimation of corn-meal in flour. A number of small samples, about 0.0039 gram each, are treated under the microscope with various reagents, which serve to distinguish the grains. The number of grains of each kind in a given field is counted, the average of several samples being taken.

A Method of Analysis for Canned Condensed Milk. By F. S. HYDE. *J. Am. Chem. Soc.*, 21, 439–444.—The author describes in detail the method used by him which consists in general in diluting the sample with a known quantity of water until it has about the consistency of cow's milk, weighing out aliquot parts of this stock solution, and applying the ordinary methods of milk analysis. A table of results is appended.

G. W. ROLFE, REVIEWER.

The Influence of Temperature on the Specific Rotation of Sucrose and Method of Correcting Readings of Compensating Polariscopes Therefor. By HARVEY W. WILEY. *J. Am. Chem. Soc.*, 21, 568–596.—This important investigation is on the influence of temperature on sugar polarizations between 4° and 40° C. The constant correction factor is in close agreement with those obtained by Andrews and the U. S. Coast and Geodetic Survey, and only slightly less than that given by Landolt and Schönrock. It would seem from the amount of data now at hand that the table of temperature corrections for polarizations compiled by the author could be adopted generally in commercial and scientific work, and it undoubtedly will be. However, the statements of the data given for the light factor of the Ventzke saccharimeter require fuller explanation lest false conclusions be drawn and the work of former accurate observers be discredited. It should have been stated that there are three figures, representing the light factor of the Ventzke saccharimeter, any one of which is correct, according to the conditions of measurement. The one last given by Landolt, 0.3468–9, represents the equivalent of one division of the new Ventzke saccharimeter whose graduation is based on 26.048 grams of cane-sugar dissolved in 100 "*true*" centimeters when this is measured in angular degrees of rotation of the light of a sodium flame

made as monochromatic as possible by filtration through a Landolt-Lippich ray filter; but if ninety-nine out of a hundred of the Ventzke instruments in the laboratories of the country were compared in this manner, the factor obtained would probably be 0.3461–2, since practically all of the saccharimeters in common use are graduated for 26.048 grams of cane-sugar in 100 "*Mohr centimeters*" at 17.5° C., an "urnormal" plate on these Ventzke instruments reading some two-tenths of a division higher than its recorded value. Finally if the angular measurement in the last case is made on a Laurent polariscope as is common, or a Wild, both of which instruments use a sodium flame filtered through bichromate only, the factor becomes 0.3455–7. Clearly for the conditions defined these factors are equally correct. By the work of many independent investigators, the third factor seems to be established beyond question as a reliable constant for the light ray obtained by the Laurent and Wild apparatus, notwithstanding that Landolt and Lippich have pointed out that defective construction is more liable to make the Laurent instrument inaccurate than some others. However, the question which is important to the analyst is not what is the best standard of light measurement to be eventually adopted by all as more closely conformable to the absolute theoretical standards, but what factor applies to the instruments he is using. In the majority of cases this is obviously the last. It is interesting to note that in the various works published in the last few years, all these light factors can be found, some one of them in each instance being given without comment as the correct value.

Xanthene Bases in Sugar Cane. By Edmund C. Shorey. *J. Am. Chem. Soc.*, **21**, 609–612.—The author finds traces of guanine in Hawaiian cane juices, and finds that this body is unchanged in the process of sugar manufacture and hence has a tendency to accumulate in the final molasses. As guanine combines with cuprous oxide, the author thinks that in the case of very low-grade products this might introduce an error if the copper is not redissolved as in the electrolytic process. He also points out that guanine may be estimated as a peptone or amide if precautions are not taken.

Report on Sugar Analysis. By R. S. Hiltner. *Proc. Assoc. Offic. Agr. Chem., Bull. U. S. Dept. Agr.*, **56**, 87–96.—The author recommends (1) that the Carr and Sanborn method for the determination of water in molasses, etc. be adopted; (2) that the quartz sand method be optional, however; (3) that the density method be restricted to high-grade products; (4) that the directions of the Lucien method for ash be revised; (5) that the Formanek be the only electrolytic method used in determining reducing sugars; (6) that in the directions for the perman-

ganate method for reducing sugars the number of grams of permanganate used be stated; and (7) that the Creydt method for the determination of sucrose and raffinose be adopted provisionally.

INORGANIC CHEMISTRY.

HENRY FAY, REVIEWER.

On the Color of Compounds of Bromine and Iodine. By J. H. KASTLE. *Am. Chem. J.*, 21, 398–413.—The color of the compounds of the halogens is discussed, and it is shown that the power of producing color increases from fluorine to iodine. It is shown that the compounds having the least color are most stable, while the colored compounds are usually easily decomposed, giving rise to colors which are similar to the color of the halogen in the free state. On heating a colored compound the intensity of the color is increased and the reverse process takes place on cooling. The author assumes that in colored compounds there is slight dissociation of the solid substance, the color being due to small quantities of the free halogen. The property of color in the halogen compounds is supposed to be an additive and not a constitutive property. Examples of a large number of inorganic and organic halogen compounds are given. Among the aromatic organic compounds it is shown that the color varies with the stability of the compound. Substitution of halogens in the benzene ring produces stable compounds, and they are usually colorless, while the side-chain substitution products are usually colored and are more unstable.

The Action of Ammonia and Amines on Chlorides of Silicon. By FELIX LENGFELD. *Am. Chem. J.*, 21, 531–537.—On bringing together benzene solutions of ammonia and silicon tetrachloride, silicon tetramide, $Si(NH_2)_4$, is formed. This substance breaks down, rapidly with water and more slowly in the air, with loss of ammonia into silicon diimide, $Si(NH)_2$. It had generally been believed that the product of the action of ammonia on silicon tetrachloride was the compound $SiCl_4.6NH_3$, but the author considers it a mixture of silicon diimide and ammonium chloride, the composition of the mixture being represented by the formula $Si(NH)_2.4NH_4Cl$. Silicon tetrethylamine is a colorless oil that does not solidify in a freezing-mixture. It keeps indefinitely in closed tubes, is decomposed by water, and boils at 102° under a pressure of 20 mm.

The Action of Chromic Acid on Hydrogen. By CHAS. L. REESE. *Am. Chem. J.*, 22, 158–164. Hydrogen is oxidized by a saturated chromic acid solution in presence of a porous ma-

terial like platinized asbestos, burnt clay balls or balls made of gypsum, but pure chromic acid does not oxidize hydrogen even in the presence of considerable quantities of sulphuric acid. The oxidation of hydrogen takes place at and above 61° when heated for a sufficient length of time; but at 50° the absorption is very slight, even after two hundred and eighty-eight hours, and at 40° there is no oxidation. Saturated solutions of chromic acid evolve oxygen freely at 119° and above, and as hydrogen is oxidized at temperatures below those at which oxygen is given off, the oxidation of hydrogen seems not to be dependent upon the evolution of oxygen from chromic acid by heat. Electrolytic hydrogen produced by passing a current through a chromic acid solution, is not oxidized by pure chromic acid, but is readily oxidized in the presence of other substances. When sulphuric acid or sulphates are added, oxidation takes place up to a certain limit, depending upon the percentage of sulphuric acid, and then ceases entirely.

Dehydration of Crystals of Sodium Phosphate. By T. C. Whitlock and C. E. Barfield. *Am. Chem. J.*, 22, 214–215. The water of constitution of disodium hydrogen phosphate begins to be lost at 230°; below this temperature water of crystallization may be determined.

Solubility of Lead Sulphate in Ammonium Acetate. By J. C. Long. *Am. Chem. J.*, 22, 217–218.—Approximate values of the solubility of lead sulphate in ammonium acetate solution are given.

Classifications of the Carbides: Their Modes of Formation and Reactions of Decomposition. By J. A. Mathews. *J. Am. Chem. Soc.*, 21, 647–650.—The author has classified the carbides according to their arrangement in the periodic system, their decomposability by water, their reaction with the halogens or halogen acids, and their behavior toward heat and oxidizing agents. The different methods of preparation and the products of decomposition which serve as a means of classification, are given.

Preparation of Graphitoidal Silicon. By Frederick S. Hyde. *J. Am. Chem. Soc.*, 21, 663–665.—The method depends upon the reduction of finely pulverized white sand with magnesium powder and the subsequent fusion of the reduction-product with cryolite and aluminium, thus forming an alloy of aluminium and silicon, from which the latter is obtained on treatment with hydrochloric acid.

Action of Hydrochloric Acid Gas upon Sulphates, Selenates, Tellurates, and Phosphates. By Raymond W. Tunnell and Edgar F. Smith. *J. Am. Chem. Soc.*, 21, 929–932.—Hydrochloric acid completely removes selenium and tellurium from the mixture of selenic or telluric acids with phosphoric acid, but will not separate these elements from sulphuric acid, some of the latter always being carried over. It was found that dry hydrochloric acid passed over dry potassium sulphate in the cold, combined with the latter, and the product formed maintained its composition at 130° and did not lose in weight when kept over soda-lime in a vacuum desiccator for fifteen hours. When dry potassium sulphate was heated in dry hydrochloric acid gas from 200° to a dull red heat, sulphuric acid was found in the receiver, while the substance remaining behind after this treatment weighed more than the original substance.

The Precipitation of Copper by Zinc. By John C. Shengle and Edgar F. Smith. *J. Am. Chem. Soc.*, 21, 932–933.—The precipitation of copper by zinc was found to give fair quantitative results, but some zinc was always found in the copper.

The Persulphates of Rubidium, Cesium, and Thallium. Arnott R. Foster and Edgar F. Smith. *J. Am. Chem. Soc.*, 21, 934–936.—These salts were prepared by electrolyzing a mixture of two parts sulphuric acid (sp. gr. 1.35) with one part of a saturated solution of the sulphate. It was impossible to isolate the thallium persulphate on account of its great solubility and the rapidity with which it decomposed in the air.

BIOLOGICAL CHEMISTRY.

A. G. Woodman, Reviewer.

Saw Palmetto. By P. L. Sherman and C. H. Briggs. *Pharm. Archives*, 2, 101–116.—The oil extracted by pressure from the fruit of the saw palmetto and also that expressed from the nuts were examined in order to ascertain their composition. The oil obtained from the pulp of the fruit was distilled under reduced pressure and found to consist of caproic, caprylic, capric, lauric, palmitic, and oleic acids and their ethyl esters, about 62 per cent. of the oil being free acids and 37 per cent. esters. The oil of the nuts contained only 2.3 per cent. free acids, the greater part of it being the glycerides of the same acids as the pulp oil with the addition of stearic acid and without the caproic acid. No alkaloids were found and the fruit was found to contain 5.4 per cent. of invert sugar.

Improvement in the Chemical Composition of the Corn Kernel. By C. G. Hopkins. *Ill. Agr. Expt. Sta., Bull.* 55, 205–240.—Experiments have been made with the object of improving the composition of the grain. The results which have been thus far obtained indicate that it is possible to bring this about by proper selection of the seed. The proportion of protein, fat, or carbohydrate may be increased or diminished at will. The fat content of the grain seems to be more susceptible to the influence of seed selection than is the protein content.

A Chemical Study of Wheat. By G. B. Frankforter and E. P. Harding. *J. Am. Chem. Soc.*, 21, 758–769.—The authors have studied wheat oil, determining some of the usual analytical constants. By extracting the saponified oil with ether and also by a new method involving the elaidin reaction a form of cholesterol, corresponding closely to paracholesterol, was obtained.

Egg Albumin. By Thomas B. Osborne. *J. Am. Chem. Soc.*, 21, 477–485.—Crystallized egg albumin, prepared by the addition of hydrochloric or acetic acid and ammonium sulphate to egg white, was purified by recrystallization and dialysis and analyzed. The results obtained furnish additional evidence that egg albumin as usually prepared is a mixture of two protein substances found in egg white.

On Some Definite Compounds of Protein Bodies. By Thos. B. Osborne. *J. Am. Chem. Soc.*, 21, 486–493.—By the use of various indicators it is shown that many of the forms of protein as usually hitherto prepared are either chemical compounds of the protein substance with ordinary mineral acids, or at least contain such compounds. This subject has been investigated more especially in the case of edestin, the mono- and bihydrochlorates of which have been prepared and studied.

The Physiological Effect of Creatin and Creatinin and Their Value as Nutrients. By J. W. Mallet. *U. S. Dept. Agr., Bull.* 66, 1–24.—A study of the chemical and physical properties of creatin and creatinin made on considerable quantities of the pure substances showed some disagreement with the description given in text-books. Determinations of the molecular heat of combustion made by Atwater gave 559 calories for creatin and 517.9 calories for creatinin. Before carrying out the physiological experiments a method was worked out and used for the quantitative separation of creatin, creatinin, and urea, which gave fairly good results. In the physiological experiments the rates of the pulse and the respiration, the body temperature,

and the reaction of the urine were observed at definite intervals. The amounts of creatin, creatinin, and urea in the excreted urine were determined. The principal conclusion derived from the results obtained is that the flesh bases do not undergo metabolism in the body, but are for the most part eliminated by way of the kidneys. Creatinin is excreted unchanged, while creatin is very largely converted to creatinin. Creatin and creatinin, then, although occurring in food, are to be disregarded as sources of energy, being eliminated from the body practically unchanged.

The Toxic Action of Sodium Fluoride. By Herbert B. Baldwin. *J. Am. Chem. Soc.*, 21, 517–521.—The author mentions several recent cases of ill effects resulting from the use of sodium fluoride and cites the work of a number of investigators, which goes to show that sodium fluoride belongs to the class of the less violent poisons.

Food Products. By A. L. Winton and Others. *Conn. Agr. Expt. Sta., Ann. Rep.* 22, *Part II*, 106–223.—This is a report of the results obtained in the analysis of various food products offered for sale throughout the state, with a description of the analytical methods employed.

The Chemical Composition of American Food Materials. By W. O. Atwater and A. P. Bryant. *U. S. Dept. Agr., Bull.* 28 (Rev. Ed.), 1–87.—This bulletin contains the maximum, minimum, and average analyses of all available American food products up to Jan. 1, 1899, with the exception of milk, butter, and other dairy products, and of sugars. The literature of the subject has been thoroughly gone over, and the tables of analyses will be found quite complete.

Some Nevada Soils. By N. E. Wilson. *Nev. Agr. Expt. Sta., Bull.* 39, 1–30.—This bulletin contains the results of analyses of twenty-six samples of representative Nevada soils.

Notes on Alkali Soil in Montana. By F. W. Traphagen and W. M. Cobleigh. *J. Am. Chem. Soc.*, 21, 753–757.—The alkali found in the Montana soils consists almost entirely of sulphates, mainly sodium sulphate. This alkali is ordinarily concentrated in a zone at a considerable depth, but when irrigation is employed the salts begin to rise to the surface and cause damage to the crops. When, however, the soil is underlain with gravel the alkali does not rise, showing that the best remedy consists in underdrainage.

Commercial Fertilizers. *Vt. Agr. Expt. Sta., Bull.* 69, 41–53; 70, 55–68; 71, 71–116; *Tex. Agr. Expt. Sta., Bull.* 51, 24–37; *R. I. Agr. Expt. Sta., Bull.* 56, 1-9; *Ky. Agr. Expt. Sta., Bull.* 82, 15-32.

G. W. ROLFE, REVIEWER.

The Sugar Beet in Maryland. By H. W. WILEY. *Md. Agr. Expt. Sta., Bull.* 61, 169–186.—The author reviews the history of the experimental work done in the state, and concludes that "in the present state of the sugar industry it has been established that Maryland cannot successfully compete in the manufacture of beet-sugar with more favorable localities in the United States."

Sugar as Food. By MARY HINMAN ABEL. *Farmers' Bull. U. S. Dept. Agr.*, 93, 7–26.—This bulletin treats in a popular way of the composition, sources, food value, and practical use of cane-sugar.

Variations in the Analyses of Cane Ashes. By ROBT. HALL. *La. Planter*, 23, 179–180.—The extraordinary variations in the amount of fertilizing constituents, especially potash, shown by published analyses, are pointed out.

The Field of Chemical Improvement in the Manufacture of Cane Sugar. By WILFRED SKAIFE. *La. Planter*, 23, 107–109.—The author reviews some of the great problems of sugar manufacture from field to finished product.

[Contribution from the Massachusetts Institute of Technology.]

REVIEW OF AMERICAN CHEMICAL RESEARCH.

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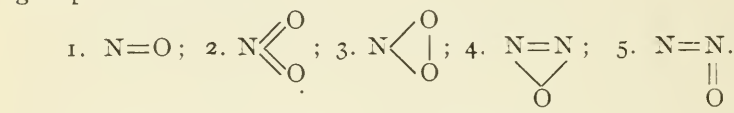
Arthur A. Noyes, Editor.
Reviewers: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby and M. L. Fuller; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Technical Chemistry, A. H. Gill and F. H. Thorp.

ORGANIC CHEMISTRY.

J. F. Norris, Reviewer.

Trinitrophenylmalonic Ester. By C. Loring Jackson and J. I. Phinney. *Am. Chem. J.*, 21, 418–433.—Trinitrophenylmalonic ester, as prepared by Jackson and Soch (*this Rev.*, 2, 10), crystallizes from alcohol in slender, rectangular needles, which melt at 58°. When precipitated from its ammonium salt and recrystallized the ester is obtained in kite-shaped crystals, which melt at 64°. The low-melting crystals are readily changed into the high-melting variety by melting, and by inoculating a saturated solution of them with a crystal of the form melting at 64°. After the high-melting crystals were once obtained it was found difficult to prepare the unstable form, as the dust of the former in the laboratory influenced the crystallization of the compound. It was found impossible to convert the stable into the unstable form. The two compounds were not polymeric modifications, as the new body was shown to have a simple molecular weight. Alkalies give with the ester melting at 64° dark-red salts, which crystallize well. The barium, strontium, calcium, zinc, cadmium, copper, and lead salts are highly-colored precipitates. When the ester was treated with concentrated nitric acid on the steam-bath, a nitrite was formed of the formula $C_6H_2(NO_2)_3CONO(CO_2C_2H_5)_2$ (m. p. 109°). By long-continued action of nitric acid, trinitrophenyltartronic ester (m. p. 167°) results, which is converted into an acetyl derivative (m. p. 125°) when heated in a sealed tube with acetyl chloride. Trinitrophenylacetic acid (m. p. 161°) was formed when the trinitrophenylmalonic ester (m. p. 64°) was saponified with sulphuric acid.

The Relation of Trivalent to Pentavalent Nitrogen. By Arthur Lachman. *Am. Chem. J.*, 21, 433–446.—In order to get some experimental evidence for the structure of nitro and azoxy compounds, a number of substances containing these groups, as well as nitroso compounds, were subjected to the action of zinc ethyl. The structures usually assigned to these groups are as follows:



If nitro and azoxy groups have the structure of formulæ 2 and 5, respectively, compounds containing them should show some resemblance to nitroso compounds (formula 1); whereas, if formulæ 3 and 4 are correct this similarity should be lacking. Diethylnitrosamine and phenylmethylnitrosamine do not react with zinc ethyl. Diphenylnitrosamine, however, which contains two aromatic groups, reacts with violence. The resulting product, which contains the amine and zinc alkyl in equal molecular quantities, decomposes with water and diphenylamine, $\beta\beta$-diethylhydroxylamine, and zinc hydroxide are formed. It is seen, therefore, that the reactive power of the nitroso group is determined by the nature of the groups with which it is united. The reaction between zinc ethyl and nitrosobenzene is a violent one, the chief reaction-products being azoxybenzene and phenylhydroxylamine. A small amount of aniline and ethylaniline is formed, but no diethylaniline could be found. Azoxybenzene does not react with zinc ethyl after long standing; it, therefore, probably has the formula usually assigned to it (number 4). Three nitro compounds were studied. Dimethylnitramine does not react with zinc ethyl; nitroethane readily forms an addition-product, which gives trimethylamine oxide, as pointed out by Bewad, and nitrobenzene reacts but slightly, the bulk of the reaction-product being a neutral, sticky mass of disagreeable character. Taking into consideration the above facts and the general result reached with the nitroso compounds, *viz.*, that negativity and reactiveness are proportional, the conclusion is drawn that nitrobenzene and nitroethane are differently constituted, the former showing the grouping represented by formula 3 above, while the latter contains a pentavalent nitrogen.

Some Derivatives of Camphoroxime. By G. B. Frankforter and A. D. Mayo. *Am. Chem. J.*, 21, 471–473.—Acetyl camphoroxime, $C_{10}H_{16}NO(CH_3CO)$ (b. p. 170°), is formed when camphoroxime is allowed to stand with acetic anhydride. If heat is applied the nitril $C_{10}H_5N$ results. With

chloral, in ethereal solution, the reaction-product is chloral camphoroxime $(C_{10}H_{16}NO)_2CHCCl + 2H_2O$, a crystalline powder which melts at 82° and decomposes spontaneously. Succinylcamphoroxime boils with decomposition at 246° and decomposes on standing.

Camphoroxime Derivatives. By G. B. Frankforter and P. M. Glasoe. *Am. Chem. J.*, 21, 474–478.—Phthalic anhydride reacts with camphoroxime in boiling benzene to form an ester which melts with decomposition at 135.5°. Camphorformaldoxime, $C_{10}H_{16}NO.CH_2OH + H_2O$ (m. p. 62°–63°), was prepared by boiling the oxime with an aqueous solution of formic aldehyde and treating the resulting oil with a large quantity of water for several days. If the oil obtained as above is exposed to the sunlight, a part of it is changed into camphorparaformaldoxime, $C_{10}H_{16}N(C_3H_5O_3)$. Monochlorcamphoroxime (m. p. 290°) was formed when an ethereal solution of the oxime was treated with sulphothionyl chloride.

The Composition of Nitrogen Iodide and the Action of Iodine on the Fatty Amines. By James F. Norris and Arthur I. Franklin. *Am. Chem. J.*, 21, 499–510.—Iodine readily reacts with triethylamine. In ethereal solution triethylamine hydroiodide and the periodide, $(CH_3)_3N.HI.I_2$, are formed; in aqueous solution iodoform is one of the products of the reaction. Tripropylamine forms an addition-product of the formula $(C_3H_7)_3N.I_2$ (m. p. 66°), analogous to the trimethylamine compound already described, and a periodide containing three iodine atoms. With diethyl, diamyl, and methylamine the products were periodides and hydroiodides. From the above facts the conclusion is drawn that iodine readily attacks the amines, causing substitution, and that this is accompanied by the formation of an addition-product of iodine and the amine only in the case of tertiary amines. This conclusion is inconsistent with the formula of nitrogen iodide, $NH_3.I_2$, recently put forward by Chattaway (*J. Chem. Soc.*, 69, 1572). A number of the arguments adduced in favor of the above formula are answered. The compound prepared by Guthrie (*J. Chem. Soc.*, 1, 239) and by Seamon (*Chem. News*, 44, 188), and to which the formula $NH_3.I_2$ was assigned, is probably a mixture of nitrogen iodide and ammonium periodide. This was shown by studying, side by side, the solubility in a number of solvents of such a mixture and the substance prepared as directed by the above authors.

On the Action of Sodic Ethylate on Tribromdinitrobenzol. By C. Loring Jackson and Waldemar Koch. *Am. Chem. J.*, 21, 510–528.—The constitution of the dinitroresorcinediethyl ether melting at 133°, formed by the action of a hot solution of

sodium ethylate on tribromdinitrobenzene ($Br_3$1,3,5,(NO_2)$_2$2,4), or on the bromdinitroresorcinediethyl ether melting at 184°, was determined by saponifying the ether to the corresponding dinitroresorcine, which proved to be the symmetrical compound (OH)$_2$1,5,(NO_2)$_2$,2,4. It follows that the bromine replaced by hydrogen in tribromdinitrobenzene is the one between the two nitro groups, and that the bromdinitroresorcinediethyl ether melting at 184° has the constitution (OC_2H_5)$_2$1,5,Br3,(NO_2)$_2$2,4. An isomeric ether, in which the bromine is not in the ortho position to two nitro groups, gave no replacement of the atom of bromine by hydrogen when treated with sodium ethylate, but gave dinitrophloroglucinetriethyl ether by the replacement of the bromine by an ethoxy group. As a result of the action of sodium ethylate on tribromdinitrobenzene (m. p. 192°) at ordinary temperature in benzene or alcohol solution, the following substances were formed: Two bromdinitroresorcinediethyl ethers, (OC_2H_5)$_2$1,5,Br3,(NO_2)$_2$2,4 (m. p. 184°), and (OC_2H_5)$_2$1,3,Br5(NO_2)$_2$2,4 (m. p. 92), tribromnitrophenol, $Br_3$1,3,5,$NO_2$2,OH4 (m. p. 90°), dinitroresorcineethyl ether, (OC_2H_5)1,OH5,(NO_2)$_2$2,4 (m. p. 77°), and dinitrophloroglucinetriethyl ethers, (OC_2H_5)$_3$1,3,5,(NO_2)$_2$2,4. The most striking phenomenon in the action of sodium ethylate on tribromdinitrobenzene at 70° is the replacement by hydrogen of the atom of bromine in the ortho position to both nitro groups, a reaction that takes place to but a slight extent in the cold. The absence of dinitrophloroglucinetriethyl ether when the reaction takes place at 70° is also noteworthy. The mechanism of all the reactions mentioned is explained at length but the discussion cannot be briefly abstracted.

The Action of Sulphocarbanilide on Certain Acid Anhydrides. By Frederick L. Dunlap. *Am. Chem. J.*, 21, 528–531.—When equal molecular quantities of sulphocarbanilide and maleïc anhydride were intimately mixed and heated to 80°–95°, diphenylthiomaleïnuric acid,

$$HOOCCH : CHCONC_6H_5CSNHC_6H_5,$$

(m. p. 160°) was formed by the direct addition of the two reacting substances. The acid forms crystalline barium, calcium, silver, potassium, and sodium salts. With succinic and phthalic anhydrides no addition-product could be isolated, however. Succinanilic acid, the product of the reaction with the corresponding anhydride, crystallizes from water in prisms which melt at 144.5°–145.5°.

Optical Rotation of Pinen Hydrochloride. By J. H. Long. *J. Am. Chem. Soc.*, 21, 637–642.—It is shown that the effect of temperature on the preparation of pinen hydrochloride from tur-

pentine is unimportant, since the compound prepared below 0° had the same specific rotation as that prepared at 40°. The author holds that turpentine obtained from one tree contains both *d*- and *l*-pinen, and that the different values of the optical rotation of pinen hydrochloride obtained by different observers, are due to the varying proportions of the two varieties in the oils investigated. It is also shown that the separation of *d*- and *l*-pinen cannot be effected by the fractionation of the compounds themselves or their hydrochlorides. The rotation of the hydrochloride prepared from *l*-pinen is greater than that of *l*-pinen, whereas the rotation of the hydrochloride of *d*-pinen is probably somewhat less than that of *d*-pinen. It follows, therefore, that when a *d*-pinen containing some *l*-pinen is treated with hydrochloric acid the rotation of the resulting compound may be reduced to zero. These facts explain the statement of Wallach and Conrady that *d*-pinen is rendered inactive by hydrochloric acid.

Camphoric Acid (Sixth Paper). By William A. Noyes. *Am. Chem. J.*, 22, 1–5.—The incorrectness of Collie's formula for camphoric acid was established by showing that cis-camholytic acid (isolauronolic acid) and Δ^1-tetrahydroxylic acid, $C_6H_6.CH_3(1).COOH(2).CH_3(3)$, are not identical. The neighboring xylic acid was reduced with sodium and amyl alcohol and the corresponding hexahydroxylic acid (m. p. 72°, b. p. 250°–252°) obtained to the extent of about 50 per cent. of the theoretical yield. By treating the reduced acid with phosphorus pentachloride and bromine the chloride of α-bromhexahydroxylic acid, $C_6H_5.CH_3(1).Br.COOH(2).CH_3(3)$, was obtained. This compound is quite stable toward water, is not readily effected by dilute sodium hydroxide, but is decomposed when warmed with glacial formic acid, from which the acid crystallizes in leaflets which melt at 150°–151°. When the α-brom acid is warmed with alcoholic potassium hydroxide, Δ^1-tetrahydroxylic acid is formed, which melts at 89°–90° after crystallization from ligroin. This acid differs from other acids of similar structure in that it is not readily oxidized by potassium permanganate.

On Undecylamine and Pentadecylamine and the Preparation of the Higher Amines of the Aliphatic Series. By Elizabeth Jeffreys. *Am. Chem. J.*, 22, 14–45.—Some time ago Lengfeld and Stieglitz (*Am. Chem. J.*, 16, 270) showed that sodium methylate in methyl alcohol solution converts acid bromamides into urethanes according to the reaction

$$RCONHBr + CH_3ONa = RNHCOOCH_3 + NaBr.$$

The author shows that the resulting urethanes are converted quantitatively into amines when distilled with slaked lime, and

that the reaction serves as an excellent method of preparing the higher aliphatic amines, which are obtained with difficulty by the older methods. The process is a simple one, since the urethanes are obtained without the isolation of the brom- or chloramides by the action of a sodium alcoholate on a mixture of the acid amide and bromine. The method is applicable to the preparation of both aliphatic and aromatic urethanes, in ethyl and methyl alcohol solution, but cannot be used when the acid amide is unsaturated or otherwise very susceptible to bromine. The amines obtained by this method were shown to be primary monoalkyl amines by the preparation of a mustard oil and an isocyanate from pentadecylamine, and by the formation of primary alcohols when sodium nitrite was allowed to act upon the amine hydrochlorides. In the preparation of the higher amines by the Hofmann reaction acyl alkyl ureas are formed to a large extent. This is shown to take place whenever, owing to the slowness of the reaction, considerable unchanged acid amide is present, while the remainder of the acid amide is suffering rearrangement; the rearranged portion then reacts with the unchanged amide even in the presence of alcohol or water and forms a urea. This is remarkable, inasmuch as isocyanates, the probable intermediate products in the Beckmann rearrangement, under ordinary circumstances do not act upon an acid amide in the presence of alcohol or water. Palmitic chloramide (m. p. 70°–71°), prepared by the action of sodium hypochlorite on palmitic amide, was obtained as a white precipitate and converted by sodium methylate into methyl pentadecylurethane which crystallizes in leaflets melting at 61°–62°. This compound, as well as methyl phenylcarbamate and methyl *m*-nitrophenylcarbamate were prepared from the amides directly by the action of a mixture of bromine and sodium methylate. Normal pentadecylamine hydrochloride, prepared from the free amine (obtained by distilling pentadecylurea with lime), crystallizes in leaflets which decompose at 200° without melting. The chlorplatinate decomposes at 205°. The corresponding urea (m. p. 109°) was prepared from the hydrochloride and potassium cyanate. Pentadecylamine crystallizes in leaflets, melts at 36.5°, boils at 298°–301°, and rapidly absorbs carbon dioxide and water. Its benzoyl derivative melts at 78°. The amine was shown to be a primary one by the action of carbon disulphide, phosgene, and sodium nitrite. In ether solution carbon disulphide gave pentadecylamine pentadecyldithiocarbamate (m. p. 99°) which, when heated in a sealed tube, was converted into dipentadecylthiourea (m. p. 88.5°). Pentadecyl mustard oil was prepared in impure condition by heating pentadecylamine, in solution in absolute alcohol, with an excess of carbon disulphide. The mustard oil was identified by treating it with aniline, when phenylpenta-

decylthiourea (m. p. 79°) was obtained. By the action of phosgene on the amine hydrochloride pentadecylurea chloride, $C_{15}H_{31}NHCOCl$, was obtained. The compound is unusually stable for substances of this class; it can be heated for several hours at 100°–150° without losing all of its hydrogen chloride. Pentadecylisocyanate (m. p. 8°–14°) was prepared by dissolving the urea chloride in benzene and heating it with calcium oxide. Dipentadecylurea (m. p. 113°) was obtained by heating the isocyanate with pentadecylamine. With sodium nitrite pentadecylamine hydrochloride gave a mixture of the corresponding alcohol and the hydrocarbon $C_{15}H_{30}$. Pentadecylphenylcarbamate (m. p. 72°) was formed when the alcohol and phenyl isocyanate were allowed to stand together. In order to find whether the methods described for obtaining urethanes and amines are general for amides of high molecular weight, the same reactions were carried out with stearic and lauric amides. The preparation of the following compounds showed that the reactions are general: Stearic chloramide (m. p. 63°–64°), methyl heptadecylcarbamate, heptadecylamine, methyl undecylcarbamate (m. p. 45°–47°), undecyllaurylurea (m. p. 105°), undecylamine hydrochloride, undecylamine chlorplatinate decomposing at 190°, normal undecylamine (m. p. 15°, b. p. 232°), benzoylundecylamine (m. p. 60°), normal undecyl alcohol (m. p. 19°, b. p. 131° at 15 mm.), undecylphenylcarbamate (m. p. 62°), undecylene (b. p. 84° at 18 mm.), and undecylene dibromide (b. p. 161° at 18 mm.).

On Certain Derivatives of Symmetrical Trichlorbenzol. By C. Loring Jackson and F. H. Gazzolo. *Am. Chem. J.*, 22, 50–61.—In a previous paper Jackson and Calvert (*this Rev.*, 2, 76) showed that when tribromiodobenzene, $Br_3$1,3,5,I2, and tetrabrombenzene, $Br_4$1,2,3,5, were treated with sodium ethylate, the halogen in position 2 was replaced by hydrogen. The investigation of the corresponding trichlor derivatives has now been made. Trichloriodobenzene, $Cl_3$1,3,5,I2 (m. p. 55°) and sodium ethylate gave symmetrical trichlorbenzene. With fuming nitric acid trichlordinitrobenzene (m. p. 129°) was formed, iodine being set free. Trichlorbrombenzene, $Cl_3$1,3,5,Br2, melts at 65°, loses bromine with sodium ethylate, and with fuming nitric acid gives trichlorbromdinitrobenzene, melting at 175°, which is a decidedly reactive substance. Aniline replaced three atoms of chlorine, giving trianilidobromdinitrobenzene melting at 175°–176°. With sodium ethylate a number of compounds are formed, from which bromdinitroresorcinediethyl ether (m. p. 81°–82°), having the probable structure $(C_2H_5O)_2$1,3, Br2$(NO_2)_2$4,6, was separated in pure condition. The formation of this compound is interesting in that it is the first case noted

in which chlorine has been replaced by hydrogen under these conditions.

Narcotine and Narceine. By George Bell Frankforter and Frank H. Keller. *Am. Chem. J.*, **22**, 61–67.—The authors doubled the yield of narceine obtained from narcotine-methyl iodide by converting the latter into the chloride by means of chlorine water instead of silver chloride. The secondary product obtained when the old method is used is probably the compound $C_7H_6(CH_3)_2N_3Cl.2AgI$. When chlorine water is used the by-product of the reaction is narcotine-methyl triiodide $C_{22}H_{27}I_2NO_7CH_3I$ (m. p. 149°). When this compound is treated with an excess of chlorine water, methylnornarcotine-methyl triiodide, $C_{20}H_{27}I_2NO_7.CH_3I$ (m. p. 186°), is formed. Narcotine methyl chloride forms a double salt with platinic chloride, which melts at 221°.

The Reaction between Aliphatic Sulphocyanates and Metallic Derivatives of Acetoacetic Ester and Analogous Substances. By Elmer P. Kohler. *Am. Chem. J.*, **22**, 67–80.—The primary reaction between the metallic derivatives of the esters of ketonic acids and aliphatic sulphocyanates results in the formation of a mercaptide and a cyanogen substitution-product of the ester. The final result depends, to some extent, upon the ester, the metal, and the sulphocyanate. If the resulting mercaptide is soluble in the liquid used as a medium, it immediately reacts with the unchanged sulphocyanate to form a disulphide. A typical reaction is represented by the following equation :

$$CH_3COCNaC_2H_5COOC_2H_5 + 2C_2H_5SCN = CH_3COC(CN)C_2H_5COOC_2H_5 + (C_2H_5S)_2 + NaCN.$$

In case the cyanogen derivative formed contains hydrogen that is replaceable by metal, it passes into a metallic derivative by liberating a corresponding amount of the original ester. With sodium derivatives, the sodium mercaptides formed slowly saponify the original esters and the cyanogen derivatives resulting from the reaction. With copper derivatives the reactions are clean, as the copper mercaptides are insoluble in organic liquids and inert. The following equation represents a typical reaction :

$$4(CH_3COCHCO_2C_2H_5)_2Cu + 4C_2H_5SCN = 2(CH_3COC(CN)CO_2C_2H_5)_2Cu + 4CH_3COCH_2CO_2C_2H_5 + (C_2H_5S)_2 + 2C_2H_5SCu.$$

The reaction between copper derivatives and polysulphocyanates that have but one sulphocyanogen group with any one carbon atom, normally involves only one of the sulphocyanogen

groups; the remainder are protected by the insolubility of the resulting mercaptide. Ethylene sulphocyanate and copper acetoacetic ester, for example, in the cold, react according to the equations:

I. $(CH_3COCHCO_2C_2H_5)_2Cu + 2(CH_2SCN)_2 =$

$$2CH_3COCH(CN)CO_2C_2H_5 + \left(\begin{array}{l} CH_2SCN \\ | \\ CH_2S \end{array}\right)_2 Cu.$$

II. $$\left(\begin{array}{l} CH_2SCN \\ | \\ CH_2S \end{array}\right)_2 Cu = 2 \begin{array}{l} CH_2SCN \\ | \\ CH_2SCu \end{array} + \begin{array}{ll} CH_2SCN & CH_2SCN \\ | & | \\ CH_2—S—S—CH_2 & \end{array}.$$

The sulphocyandisulphides thus formed are soluble in organic solvents and at higher temperatures react like simpler polysulphocyanates. By adding the sulphocyanate, in very small quantities, to a saturated solution of the copper derivatives, all of the sulphocyanogen groups can be brought into reaction. When polysulphocyanates have two sulphocyanogen groups in combination with the same carbon atom, both of them enter into reaction under all conditions. A difference in behavior with copper and sodium derivatives is observed in the case of halogen substitution-products of the sulphocyanates. With the former chlorethylsulphocyanate reacts, the halogen not taking part in the reaction. With the latter, two reactions take place simultaneously—the normal reaction of the sulphocyanates and the general reaction of halogen substitution-products. Copper cyanacetoacetic ester crystallizes from alcohol in green plates, which melt with decomposition at about 250°. The compound of the formula $CuSCH_2.CH_2SCN$, formed by the action of ethylene sulphocyanate on copper acetoacetic ester, when boiled with concentrated hydrochloric acid, gives iminomethene-ethenedisulphide hydrochloride,

$$\begin{array}{l} CH_2S \\ | \\ CH_2S \end{array}\!\!>\!CNH.HCl.$$

The compound represented by the formula $(NCSCH_2.CH_2S)_2$ is a colorless liquid which does not solidify at —20° and does not boil without decomposition. When warmed with strong potassium hydroxide it is converted into ethylenetetrasulphide. The mercaptide $CuSCH_2.S.CH_2SCu$ is a light yellow impalpable powder. Cyanethylacetoacetic ester boils at 130° at 35 mm. pressure, and sulphocyanethylacetoacetic ester,

$$CH_3COC(CH_2CH_2SCN)CHCO_2C_2H_5,$$

crystallizes in colorless, transparent plates, which melt at 83°.

On Nitromalonic Aldehyde. By Henry B. Hill and Joseph Torrey, Jr. *Am. Chem. J.*, **22**, 89–110.—When mucobromic acid is added to a solution of sodium nitrite in dilute alcohol a vigorous reaction takes place with rise in temperature, evolution of carbon dioxide, and change in color of the solution to a deep red. From the cooled reaction-mixture sodium nitromalonic aldehyde, $NaC_3H_2NO_4.H_2O$, crystallizes in needles. The free aldehyde (m. p. 50°–51°) was obtained by treating its silver salt suspended in ether with an ethereal solution of hydrogen chloride. The constitution of the compound was established by the reactions and condensations of the aldehyde described below. When aniline hydrochloride was added to an aqueous solution of the sodium salt of the aldehyde, an anil was formed in which an oxygen of the aldehyde groups had been replaced by the radical $=N.C_6H_5$. The compound crystallizes in yellow scales, which melt at 143°–144°. If aniline is used the dianil (m. p. 93°–94°) results. Analogous compounds were prepared with *p*-toluidine, *o*-toluidine, methylamine, ethylamine, isoamylamine, and phenylhydrazine. The phenylhydrazone melts at 101°, and is converted by heating in alcoholic solution at its melting-point into 1-phenyl-4-nitropyrazol, melting at 126°–127°. The latter compound was also obtained where the diphenylhydrazone (m. p. 98°) was heated. The diphenylhydrazone yields stable sodium and lead salts. Hydrazine sulphate and an aqueous solution of sodium nitromalonic aldehyde produced a dark red precipitate which, when decomposed with hydrochloric acid, gave as one of the decomposition-products 4-nitropyrazol. The constitution of the phenylnitropyrazol mentioned above was thus established. In neutral solution hydroxylamine hydrochloride and sodium nitromalonic aldehyde give *β*-nitroisoxazol (m. p. 46°–47°), in alkaline solution two molecules of the hydroxylamine enter into the reaction and the sodium salt of a dioxime is formed. This sodium salt is readily converted into a silver salt, and when treated with aniline hydrochloride is changed into nitromalonic aldehyde aniloxime (m. p. 162°). Sodium nitromalonic aldehyde condenses with acetone in alkaline solution and forms a compound which yields *p*-nitrophenol. The aldehyde condenses also with methyl-ethyl ketone, giving nitro-*o*-cresol, with benzyl ketone, giving a nitrophenol derived from *m*-diphenyl benzene, with acetoacetic ester, giving nitrosalicylic acid, and with acetone dicarboxylic acid giving nitrooxyisophthalic acid. When a solution of the sodium salt of nitromalonic aldehyde was acidified with one molecular quantity of hydrochloric acid and allowed to stand some time, symmetrical trinitrobenzene crystallized out, and formic acid appeared in the solution. It seems probable that the trinitrobenzene is formed by the spontaneous condensation of nitroacetaldehyde, which is

first formed together with formic acid by the addition of water to the nitromalonic aldehyde.

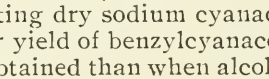
On the Rearrangement of the Thioncarbamic Esters. By H. L. Wheeler and Bayard Barnes. *Am. Chem. J.*, **22**, 141–152.—When a thioncarbamic ester, $H_2N.CS.OR$, is treated with an alkyl halide, it is converted into a thiolcarbamic ester, $H_2N.CO.SR$. This rearrangement is the result of the addition of the halide to the thion compound, either at the double bond or to the sulphur atom, and the subsequent elimination of the halogen atom with the alkyl group originally present in the thion ester. In this way methyl and ethyl thioncarbamate were changed into methyl thiolcarbamate when allowed to stand with methyl iodide. This rearrangement was shown to be a general reaction by preparing from the corresponding thioncarbamates the following thiolcarbamates: methyl (m. p. 107°–108°), ethyl (m. p. 107°–108°), isobutyl (m. p. 102°–103°), and isoamyl (m. p. 112°–113°). The isopropyl derivative (m. p. 125°) was made from the isoamyl compound. When ethyl thioncarbamate was treated with ethylene bromide both bromine atoms took part in the reaction, the ethylene ester of thiolcarbamic acid being formed. Since the alkyl halides readily change thion into thiol compounds the arguments put forward for the structure of some thiol acids, based on the action of ethyl bromide on their salts, no longer hold. The salt formed by the action of carbon oxysulphide on ammonia is probably a thion compound and not a thiol derivative, although it gives with ethyl bromide ethyl thiolcarbamate. The work suggested that a rearrangement might be effected in the case of tetravalent sulphur compounds by alkyl halides. This was found not to be the case with the esters of sulphinic acids and with alkyl sulphites.

Dimethyldianthracene: A Polymeric Modification of β-Methylanthracene. By W. R. Orndorff and H. A. Megraw. *Am. Chem. J.*, **22**, 152–157.—In a previous paper (*this Rev.*, **2**, 77) it was shown that anthracene and anthranol, when suspended in benzene and exposed to sunlight, were rapidly polymerized to compounds which had twice the molecular weight of the original substances. Under the same conditions, from β-methylanthracene a white crystalline substance is formed, which melts with slight decomposition at 228°–230° after several recrystallizations from toluene. The compound has the same percentage composition as β-methylanthracene but twice its molecular weight. It is therefore, dimethyldianthracene. The new hydrocarbon does not show the fluorescence characteristic of anthracene and methyl anthracene, and does not form an addition-compound with picric acid. It probably crystallizes in

the orthorhombic system and is changed into β-methylanthracene at its melting-point.

Action of Sulphuric Acid on Nitroheptane. By R. A. Worstall. *Am. Chem. J.*, 22, 164–167.—When nitroheptane was treated with dilute or concentrated sulphuric acid the products of the reaction were heptoic acid and ammonia. When, however, fuming sulphuric acid was used a small amount of nitroheptane sulphonic acid was also formed. The acid which could not be purified was separated by means of its barium salt, which crystallizes in small reddish-yellow plates. An attempt was made to prepare a sulphonic acid by acting upon bromnitroheptane with sodium sulphite, but without success.

On Alkyl Malonic Nitriles and Their Derivatives. By John C. Hessler. *Am. Chem. J.*, 22, 169–198.—The author describes in detail the preparation and reactions of a number of alkyl malonic nitriles and their derivatives. When sodium cyanacetic ester was treated with ethyl iodide in alcoholic solution, the yield of ethyl cyanacetic ester was 74 per cent. of the theoretical, and about one-fourth of the reaction-product was diethylcyanacetic ester. When no solvent was used the yield of the disubstitution-product was decreased about one-half. Ethylcyanacetamide (m. p. 113°, b. p. 180°–190° at 24 mm.) and diethylcyanacetamide (m. p. 122°) were prepared from the corresponding esters. Ethylcyanacetic acid is a hygroscopic liquid, which boils at 160°–161° at 24 mm. and forms a white crystalline silver salt. By treating dry sodium cyanacetic ester with ethyl iodide a much larger yield of benzylcyanacetic ester (b. p. 176°–185° at 21 mm.) is obtained than when alcohol is used as solvent. Dibenzylcyanacetic ester, which is obtained at the same time, melts at 33°. From analogy with other compounds of the same class the sodium salt of cyanacetic ester has probably the constitution represented by the following formula:



Benzylcyanacetamide (m. p. 130°) is converted into benzylmalonic nitrile (m. p. 91°) by phosphorus pentachloride. When the sodium salt of the nitrile was heated under diminished pressure hydrocinnamic nitrile was formed. The formation of an inorganic cyanide, when the sodium and silver salts of the nitrile are heated, is evidence for the following formula for the salts: $C_6H_5CH_2(CN)C{=}C{=}N.M$. The sodium and silver salts of ethylmalonic nitrile (b. p. 200°) behave in the same way when heated, but it was found impossible to separate in pure condi-

tion any organic substance formed in the decomposition. When malonic nitrile was heated with alcoholic sodium ethylate and benzyl chloride the resulting mixture of the mono- and dibenzyl substitution-products contained 90 per cent. of the latter compound. When the dry sodium salt of the nitrile was used the yield of the mono derivative was increased. Benzylcyanacetic acid melts at 101°–102° and gives a white insoluble silver salt. Benzoylbenzyl nitrile melts at 100° and is converted into benzylmalonic nitrile and ethyl benzoate when boiled with alcohol. Brombenzylmalonic nitrile (m. p. 119°–120°) was prepared by brominating sodium benzylmalonic nitrile. From the sodium salt carbethoxybenzylmalonic nitrile (m. p. 44°–45°) was prepared by the action of chlorcarbonic ether, and methylbenzylmalonic nitrile (m. p. 94°–95°) by the action of methyl iodide. By the action of methyl iodide and alcoholic sodium ethylate on benzylmalonic nitrile, methylbenzylcyanacetimidoethyl ester (b. p. 170° at 22 mm.) was formed and not the nitrile, which is usually formed by this reaction. The corresponding ethyl derivative (b. p. 170° at 22 mm.) was prepared from benzylmalonic nitrile and ethyl iodide, and from ethylmalonic nitrile and benzyl chloride. Phenylacetamidoethyl ester, prepared from the chloride by the method of Bushong, boils at 105°–106° at 10 mm. Monimidomalonic ester, made from cyanacetic ester by the method of Pinner, decomposes when heated to 165° at ordinary pressure.

On the Phenylhydrazones of Benzoin. By Alexander Smith. *Am. Chem. J.*, **22**, 198–207.—Some time ago Smith and Ransom (*Am. Chem. J.*, **16**, 108) described the preparation and properties of a substance formed by the interaction of phenylhydrazine and benzoin, which differed in physical properties, although not in chemical properties and composition, from the phenylhydrazone which was known at that time. The relation between these two bodies has been recently investigated by Freer (*this Rev.*, **5**, 32) who obtained results not in accord with those obtained by Smith and Ransom. Freer found that the bodies behave differently towards benzoyl chloride and nitrous anhydride, and from these facts came to the conclusion that the compounds are not stereoisomers, but are structurally different, one being a hydrazo derivative and the other a hydrazone. The author has repeated the work of Smith and Ransom and finds nothing to modify in their published statements. It is also shown that the substance described by Freer as *γ*-phenylhydrazone is benzanilide, and that the two phenylhydrazones of benzoin show the same behavior when treated with benzoyl chloride and with nitrous anhydride. There is no evidence, therefore, against the stereochemical explanation of the isomerism of the hydrazones.

Disulphones and Ketosulphones. By Elmer P. Kohler and Margaret B. MacDonald. *Am. Chem. J.*, **22**, 219–227. —The sodium salts of sulphinic acids react readily with acid chlorides, giving substances of a new class: with sulphone chlorides, disulphones $RSO_2—SO_2R$, and with the chlorides of the carbonic acids, ketosulphones $RCO—SO_2R$ are formed. The disulphones are remarkably inert; they are not changed by boiling with dilute acids or alkalies and can be crystallized without loss from concentrated nitric acid. They are broken down, however, when boiled with concentrated potassium hydroxide into a sulphinate and a sulphonate. Di-*p*-tolyldisulphone is insoluble in water and alcohol and crystallizes from benzene in monoclinic tables, which melt with decomposition at 212°. Phenyl-*p*-tolyldisulphone (m. p. 166°) and *p*-tolyl-*p*-nitro-*o*-tolyldisulphone (m. p. 154°) were also prepared and studied. Phenyl-*p*-tolylketosulphone, $C_6H_5CO—SO_2C_6H_4.CH_3$, formed by the action of benzoyl chloride on sodium toluenesulphinate, was found to be a very reactive substance, which formed addition-products with water, hydrogen potassium sulphite, and hydrocyanic acid, and showed the usual ketone reactions with hydroxylamine, phenylhydrazine, primary amines, and phenols. The hydrate of the compound melts at 80° and decomposes before the water is driven off.

The Reaction between Sulphone Chlorides and Metallic Derivatives of Ketonic Esters. By Elmer P. Kohler and Margaret B. MacDonald. *Am. Chem. J.*, **22**, 227–239.—The reaction between toluene sulphone chloride and the sodium derivative of acetoacetic ester is much more complicated than the analogous reaction with the chlorides of the carbonic acids. With the sulphone chloride the primary reaction consists in the interchange of sodium and chlorine with the formation of sodium toluenesulphinate and chloracetoacetic ester. The latter compound then reacts with some of the unchanged sodium derivative to form diacetosuccinic ester and sodium chloride. The chlor ester also reacts with the sodium toluenesulphinate forming toluenesulphoneacetoacetic ester, which in turn reacts with the alcohol present and forms toluenesulphonacetic ester. Although it was found impossible to isolate toluenesulphoneacetoacetic ester, its sodium derivative was prepared in small quantity as the result of a secondary reaction between the sodium derivative of acetoacetic ester and the ethyl ester of toluenethiosulphonic acid, the primary reaction being the formation of sodium toluenesulphinate, diacetosuccinic ester, and ethyl disulphide. The products of the reaction between toluenesulphone chloride and sodium malonic ester were sodium toluenesulphinate and sodium toluenesulphoneacetic acid. With disodium malonic

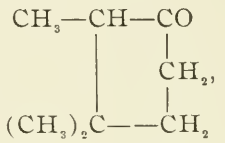
ester, a salt of the composition $C_7H_7SO_2CNa.CO_2Na.CO_2C_2H_5$ was formed, which was decomposed into toluenesulphonacetic ester by hydrochloric acid. The course of the reaction between sodium toluenesulphinate and chloracetoacetic ester was found to depend upon the temperature and concentration. In cold dilute solutions an acetyl or carbethoxyl group is replaced by the sulphone group; in boiling concentrated solutions the sulphinate is oxidized and the chlor ester reduced.

On Potassium Cyanide as a Condensing Agent. By Alexander Smith. *Am. Chem. J.*, 22, 249–256.—Condensation of benzoin with ketones is readily effected by means of potassium cyanide. The reaction takes place in alcoholic solution, but a better yield is obtained when the substances are fused with the cyanide.

Desyl-α-acetonaphthone, $\begin{matrix} C_6H_5.CH.CH_2 \\ | \quad | \\ C_6H_5.CO \quad COC_{10}H_7 \end{matrix}$, prepared from benzoin and α-acetonaphthone melts at 151°. When treated with cold concentrated sulphuric acid it is converted into diphenyl-α-naphthylfurfurane (m. p. 96°), and when heated with alcoholic ammonia in a sealed tube diphenyl-α-naphthylpyrrol (m. p. 122°) is formed. Desyl-β-naphthone melts at 155°. When benzaldehyde was heated to 150° with powdered potassium cyanide a good yield of benzoin was obtained. Desylacetophenone and desyl-α-acetonaphthone were easily prepared by condensing by means of powdered potassium cyanide or potassium hydroxide. The yield of desylacetomesitone (m. p. 115°) was 61 per cent. of the theoretical, when benzoin and acetomesitone were heated at 150° with potassium hydroxide. Diphenylmesitylfurfurane (m. p. 87°) and diphenylmesitylpyrrol (m. p. 188°) were prepared by the usual reactions from desylacetomesitone. When a fused mixture of benzyl cyanide and benzoin were heated with potassium cyanide there were obtained, in addition to the reaction-product formed when alcoholic solutions were used, benzalbenzyl cyanide, diphenylsuccinic nitrile, and a yellow amorphous substance, which was not investigated.

Camphoric Acid. By William A. Noyes. *Am. Chem. J.*, 22, 256–266.—The author shows that facts established by himself and by others indicate that the formula of camphoric acid proposed by Perkin (*Proc. Chem. Soc.*, 1896, 191) and by Bouveault, which represents the compound as a derivative of succinic acid, is probably correct. The results of a study of the ketone $C_8H_{14}O$, prepared by Noyes and Harris (*this Rev.*, 3, 12), give further evidence of the correctness of this view. The synthesis of this ketone from isoamyl bromide was attempted but has not been completed. Amyl bromide, from the amyl alcohol

of fusel oil, was converted into isocaproic acid, which was oxidized to isocaprolactone. From this compound was prepared γ-bromisocaproic ester, which yielded with sodium ethylate and cyanacetic acid a small amount of dimethylcyancarboxethylcyclopentanone, an unsaturated fatty acid being formed at the same time. This ketone melts at 148.5°, and when heated in a sealed tube with water at 150°–160° loses the cyanogen group. (With J. W. SHEPHERD.) Dihydrociscampholytic acid was converted into the chloride of the α-brom acid by treatment with phosphorus pentachloride and bromine. The ethyl ester, prepared from the chloride, was shaken with a solution of barium hydroxide. The hydroxy acid (m. p. 112°) so prepared was converted into the ketone $C_8H_{14}O$, mentioned above, by distillation with lead peroxide and sulphuric acid. The ketone boils at 167°–169° and forms an oxime which melts at 104°. It, in all probability, is a cyclopentanone, and has the formula



for it condenses with but one molecule of benzoic aldehyde to form the compound $C_8H_{12}O{=}CHC_6H_5$ (m. p. 74°).

Researches on Substitution: The Action of Bromine on Metachlor-, Metabrom-, and Metaiodoanilines. By H. L. WHEELER AND WILLIAM VALENTINE. *Am. Chem. J.*, **22**, 266–280.—When *m*-bromaniline, dissolved in glacial acetic acid, was treated with an equal molecular quantity of bromine, the product obtained in largest amount was 3,4-dibromaniline; next in amount was 3,4,6-tribromaniline; then followed 2,3,4-tribromaniline and a small quantity of 2,3,4-6-tetrabromaniline. The bromination of *m*-chlor- and *m*-iodoanilines gave similar results. It follows, therefore, when bromine acts upon aniline which contains a halogen atom in the meta position, it substitutes the hydrogen in the order 4, 6, and 2. Previous work has shown that position 6 is the most favored for an entering halogen atom in *m*-nitroaniline. As a result of the work the following substances were prepared: 3-chlor-4-bromaniline (m. p. 67°–68°) and its hydrochloride, sulphate, and picrate; nitrochlorbrombenzene, NO_2ClBr,1,4,3 (m. p. 49°–50°); 3-chlor-4-brom-2,6-dinitraniline (m. p. 169°–170°); 3-chlor-4-bromacetanilide (m. p. 125°); 3-chlor-4-brom-6-nitroacetanilide (m. p. 129°–130°); 3-chlor-4-brom-6-nitraniline (m. p. 202°–203°); 4-chlor-3-bromnitrobenzene (m. p. 60°); 4-chlor-3-bromaniline (m. p. 78°); 3-chlor-4,6-dibromaniline (m. p. 79°–80°); 3-chlor-2,4,6-tribrom-

aniline; 3,4-dibromaniline (m. p. 80°–81°) and its hydrochloride, picrate, and sulphate; 3,4,6-tribromaniline (m. p. 85°-86°); 1,3,4-tribrombenzene (m. p. 44°); 3,4,6-tribromacetanilide (m. p. 188°–189°); 3,6-dibromacetanilide (m. p. 171°–172°); 3-iod-4-bromaniline (m. p. 77°) and its hydrochloride, sulphate, and picrate; 3-iod-4-acetanilide (m. p. 138°–139°); 3-iod-4,6-dibromaniline (m. p. 81°); 3-iod-2,4,6-tribromaniline (m. p. 115°–116°).

Upon the Action of Diazo Compounds on Thymolparasulpho Acid. By James H. Stebbins, Jr. *J. Am. Chem. Soc.*, 21, 741–746.—By the action of diazonaphthionic acid on *p*-thymolsulphonic acid, a substance which had a crimson-red color and an azo compound were formed. The latter compound was isolated in the form of its barium salt, which probably has the formula $baSO_3.C_{10}H_6N{=}NC_{10}H_{12}O.SO_3ba$.

Halides and Perhalides of the Picolines. By Paul Murrill. *J. Am. Chem. Soc.*, 21, 828–854.—A large number of salts were prepared which resemble closely in composition and properties analogous compounds of this class.

An Electrolytic Study of Benzoin and Benzil. By Joseph H. James. *J. Am. Chem. Soc.*, 21, 889–911.—The electrolytic oxidation of benzoin in sodium hydroxide solution yielded benzoic acid and tarry decomposition-products. In sulphuric acid the same result was obtained, but in the presence of hydrochloric acid benzil was also formed. The electrolytic reduction of benzoin gave a body, the nature of which was not established, but which differed from the compounds formed by the reduction of benzoin by sodium amalgam or zinc and hydrochloric acid. The electrolytic oxidation of benzil gave benzoic acid when the solvent was sulphuric acid. In other cases either no oxidation took place or tarry products were formed. The electrolytic reduction of benzil in sodium hydroxide solution gave nothing definite, but in sulphuric acid a good yield of almost pure benzoin was obtained. From the above it is seen that electrolytic oxidation and reduction give practically the same result as those obtained by chemical means, but not so readily or with as good yield.

The Chromic Acid Test for Cocaine. By George L. Schaefer. *J. Am. Chem. Soc.*, 21, 936–938.—The author replies to criticisms of the test proposed by him and gives further directions for its use.

The Action of Sodium Methylate upon Dibromides of Propenyl Compounds and of Unsaturated Ketones. By F. J. Pond, O. P. Maxwell, and G. M. Norman. *J. Am. Chem.*

Soc., 21, 955–967.—In a former paper (*this Rev.*, 4, 9) it was shown that certain ethers which contain a propenyl group readily form dibromides, which are converted into ketones on treatment with sodium methylate. It is shown in the present paper that isoapiol and propyl isoeugenol undergo similar transformations and that dibromides of certain unsaturated ketones of the formula $R—CH=CH—CO—C_6H_5$ may be readily changed into 1,3-diketones.

The Electrolytic Oxidation of Succinic Acid. By Charles H. Clarke and Edgar F. Smith. *J. Am. Chem. Soc.*, 21, 967–972.—When a solution of succinic acid in sodium hydroxide or alcohol was subjected to the action of electrolytic oxygen the following substances were formed: tartaric acid, oxalic acid, oxygen, carbon monoxide, carbon dioxide, ethylene, methane, and some aromatic bodies which were not studied.

On β-Heptylamine. By Thomas Clarke. *J. Am. Chem. Soc.*, 21, 1027–1032.—β-heptylamine was prepared by heating β-heptyl bromide with ammonia in a sealed tube. Heptylene was produced as a secondary product. The hydrobromide, hydrochloride, oxalate, and double salts of the amine with platinic and auric chlorides are described.

Hydrogen Peroxide as a Test for Salicylic Acid. By W. E. Ridenour. *Am. J. Pharm.*, 71, 414–416.—A dilute solution of sodium salicylate gives a cherry-red color when treated with hydrogen peroxide in the presence of an ammoniacal solution of ammonium carbonate. One part of acid in 2,000 parts of water can be detected in this way. The conditions necessary for the reaction and a table showing the influence of a large number of chemicals are given.

Acet-*p*-sulphanilate of Sodium. By Geo. W. Funck. *Pharm. Rev.*, 17, 249–254.—The author gives a review of all the work done on the above compound. This includes a complete bibliography of the salt and an account of its history, formation, preparation, and physical, chemical, and therapeutic properties.

Acetanilide. By Charles W. Gorr. *Pharm. Rev.*, 17, 295–305.—This article consists mainly of a résumé of the present knowledge concerning the modes of formation and of preparation, and the chemical and physical properties of acetanilide.

GEOLOGICAL AND MINERALOGICAL CHEMISTRY.

M. L. Fuller, Reviewer.

Analysis and Composition [of Roscoelite]. By W. F. Hillebrand. *Am. J. Sci.*, 157, 451–454.—Samples of this

vanadium mica from Eldorado County, California, were analyzed by the author with a view of reconciling the discrepancies between the analyses of Roscoe and Genth, and of establishing a satisfactory formula. A detailed description of the methods used in the determination of vanadium is given. The analyses varied from those of Roscoe in that no manganese or calcium was found, and from those of Genth in having over three per cent. more V_2O_3.

Chemical Constitution of Roscoelite. By F. W. Clarke. *Am. J. Sci.*, 157, 454–455.—From the analysis of Hillebrand the author has calculated the empirical formula to be

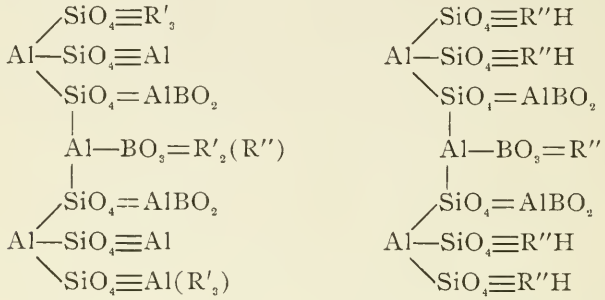
$$H_{458}K_{220}Fe_{22}Mg_{41}Al_{226}V_{318}Si_{753}O_{2724}.$$

Considering the groups SiO_4 and Si_3O_8 to be replaceable, the formula reduces to $R'_{678}R''_{62}Al_{226}V_{318}(SiO_4)_{536}(Si_3O_8)_{71}$, which would indicate, according to Clarke's mica theory, a mixture of three molecules, representing respectively a normal phlogopite, a trisilicate alkaline biotite, and a vanadium muscovite, the last forming 74.5 per cent. of the whole mass.

On the Chemical Composition of Parisite and a New Occurrence of it in Ravalli County, Montana. By S. L. Penfield and C. H. Warren. *Am. J. Sci.*, 158, 21–24.—The parisite occurs in a fine-grained, friable white substance resembling decomposed rhyolite or trachyte, and is associated with numerous pyritohedrons of pyrite. It crystallizes in rather long hexagonal shafts, made up of pyramids in oscillatory combination, and terminated by distinct, somewhat enlarged pyramids. A study of the analysis made by the authors indicates that parisite is probably a double carbonate of the formula $2(RF)CO_3.CaCO_3$ or $(RF)_2Ca(CO_3)_3$ in which R=Ce, La, Di, etc.

The Constitution of Tourmaline. By F. W. Clarke. *Am. J Sci.*, 158, 111–121.—Upon reducing to a common basis of six silicon atoms, the formula $H_{11}Al_3B_2Si_4O_{21}$ of Penfield and Foote becomes $H_{16.5}Al_{4.5}B_3Si_6O_{31.5}$, while that of Clarke is $H_{14}Al_5B_3Si_6O_{31}$. The author holds the view that these slight differences amount to no more than the uncertainties of the analyses, and in support of this view gives a series of formulæ computed from Rigg's data, which show variations beyond both extremes, and make it probable that neither formula can be accepted without qualification as final. The intimate relation of tourmaline to mica is indicated by the alteration of the former to mica, by the parallelism in composition between the two when they occur together, and by the similarity in the commingling of isomorphous molecules in the two groups. Allied to muscovite, $Al_3(SiO_4)KH_2$, is $Al_5(SiO_4)_6(BO_2)_2.BO_3H_2.H_{12}$, the tour-

maline acid, in which the H may be replaced by Ca, Mg, Na, and Al. Numerous examples of mixtures of isomorphous molecules of this tourmaline acid are given. The formulæ advanced by the author as covering all established variations in composition and rendering intelligible the various isomorphous mixtures, are as follows:



The objection to these formulæ, and also to that of Penfield and Foote as well, is that the end products contain no alkalies, while in reality an alkali-free tourmaline is unknown. Assuming these formulæ, the variations from the supposed ratio of silicon and boron of 2 : 1 are accounted for by the supposition that part of the bivalent group of atoms $=Al—BO_2$ is replaced by the similar groups $=Al—OH$ and $=Al—F$. Room for alternatives still exists, and future investigation may prove a derivation from a complex boro-silicic acid as yet unknown.

Note on a New Meteoric Iron Found near Tombigbee River, in Choctaw and Sumter Counties, Alabama, U. S. A. By Warren M. Foote. *Am. J. Sci.*, 158, 153–156.—Detailed descriptions are given of the appearance, structure, and occurrence of six masses with an aggregate weight of nearly a hundred pounds. An analysis made by Mr. J. E. Whitfield showed 95 per cent. iron, 4 per cent. nickel, with small amounts of cobalt, phosphorus, carbon, and sulphur.

An Albertite-like Asphalt in the Choctaw Nation, Indian Territory. By Joseph A. Taff. *Am. J. Sci.*, 158, 219–224.—This asphalt, which is found in several localities in the vicinity of McAllister, in the southeastern portion of the territory, occurs as stringers in veins filling fissures along zones of thrust faulting in shales of unknown age. Although an analysis showed that in composition it was very similar to certain bituminous coals of the same region, its brittleness, easy fusibility, and more especially its distillation products, show that it should be placed among the asphalts. Of these it most nearly resem-

bles albertite, the only important variation being the greater solubility of the latter in terpentine.

On the Separation of Alumina from Molten Magmas, and the Formation of Corundum. By J. H. Pratt. *Am. J. Sci.*, 158, 227–231.—The evidences bearing upon the separation of alumina from molten magmas as presented in the field by the various types of peridotites of North Carolina are discussed, and an account given of the experiments of Morozewicz and their results. The conclusions are as follows: (1) Corundum will not separate out from a calcium-sodium-potassium silicate magma unless the ratio of alumina to the other bases is more than 1 : 1 and that of silica is less than 6. (2) It will not separate unless more than enough alumina is present to unite with all the magnesia and iron in the magma. (3) All alumina in a magnesium silicate magma, if there is no excess of magnesia, will separate as corundum. (4) If magnesia is in excess, the excess will unite with alumina to form spinel, the remainder separating as corundum. (5) In the presence of chromic oxide in a magnesium silicate magma, slight amounts of alumina and magnesia unite with the chromic oxide to form chromite, but corundum and spinel do not separate. (6) In peridotite magmas containing alkalies or alkali earths a portion of the alumina unites with them to form feldspar. (7) The tendency of alumina to unite with alkalies or alkali earths to form double silicates is strong, but it has little tendency to unite with magnesia when the magma is a magnesium silicate.

Experiments Relative to the Constitution of Pectolite, Pyrophyllite, Calamine and Analcite. By F. W. Clarke and George Steiger. *Am. J. Sci.*, 158, 245–257.—The purpose of the examination was to gain evidence of the chemical structure of silicates by means of fractional analyses. 1. Pectolite. The radiated variety from Bergen Hill, N. J., was analyzed, the analysis giving the accepted formula $HNaCa_2Si_3O_9$. To determine whether this represents a true metasilicate, the mineral was ignited and afterwards boiled in a solution of sodium carbonate, with the result that a mean of 8.68 per cent. of silica (the amount proportional to the acid hydrogen) went into solution. Boiling the unignited mineral in the sodium carbonate solution, or even with water alone, resulted in a slow decomposition with loss of both silica and bases. The loss on boiling for 16 hours in distilled water was 4.09 per cent. 2. Pyrophyllite. On strongly igniting and treating with a solution of sodium carbonate, it was found that only 2.84 per cent. of silica was liberated, indicating that the mineral may with propriety be regarded as a basic salt of the acid $H_2Si_2O_5$ with the formula $Si_2O_5{=}Al{-}OH$. Pyrophyllite was only slightly attacked by heating

with dry ammonium chloride. 3. Calamine. On igniting no definite fraction of water was split off. Boiling with sodium carbonate dissolved slight amounts of silica and zinc, but no breaking up into definite distinguishable fractions occurred. The evidence, though negative, is in favor of the usual formula $SiO_5=(ZnOH)_2$. 4. Analcite. On ignition and treatment with sodium carbonate solution only a slight amount of silica was split off, indicating the absence of metasilicic acid or an acid metasilicate. On heating with dry ammonium chloride there was again very little silica split off, but half of the sodium was converted to NaCl, and part of the water replaced by NH_3, giving a residue of $H_2Na_2Al_4Si_8O_{24}.NH_3$. This points to the original formula of $Na_4Al_4Si_8O_{24}.4H_2O$, which is contrasted with the usual formula $NaAlSi_2O_6.H_2O$. The conclusion from the probable structural formula is that analcite is a member of the garnet-sodalite group.

The Mineralogical Structure and Chemical Composition of the Trap of Rocky Hill, N. J. By Alexander Hamilton Phillips. *Am. J. Sci.*, 158, 267–285.—Numerous analyses of the trap and of several of the component minerals are given. The trap occurs in the form of a dike and in general appearance resembles a dolerite. In composition, however, it approaches closely to diorite but with border phases allied to diabase.

Some Analyses of Italian Volcanic Rocks. I. By Henry S. Washington. *Am. J. Sci.*, 158, 286–294.—The analyses of the trachytes of the Phlegraean Fields and Ischia indicate that these volcanic rocks are not genetically related to the closely adjacent rocks of Somma and Vesuvius, but are connected with a second and older fracture line extending from Capraia to Sicily, and covered largely by the waters of the Mediterranean. The rocks of this latter fracture show an excess of Na_2O over K_2O, while in the former K_2O and CaO predominate. A third fracture line, the oldest of the three, occurs far out in the Mediterranean and is characterized by rocks very high in Na_2O and possessing several peculiar sodium minerals.

Mineralogical Notes: Melonite, Coloradoite, Petzite, Hessite. By W. F. Hillebrand. *Am. J. Sci.*, 158, 295–298.—An analysis of a nickel telluride from the Mother Lode region of California gave the formula $NiTe_2$, and is regarded by the author as probably identical with the melonite (Ni_2Te_3) of Genth, which was obtained from the same locality. Other minerals recognized from this locality were coloradoite, petzite, and hessite. Analyses are given for the last two.

An Account of the Character and Distribution of Maryland Building Stones. By EDWARD B. MATHEWS. *Maryland Geol. Surv.*, 2, 125–241 (1898).—An extended description, accompanied by colored plates, is given of the common building stones, including granite, gneiss, limestone, marble, sandstone, and slate. The descriptions of the more typical varieties are supplemented by analyses.

The Physical, Chemical, and Economic Properties of Building Stones. By GEORGE P. MERRILL. *Maryland Geol. Surv.*, 2, 47–123 (1898).—A general description of the building stones of Maryland is given, supplemented by a discussion of the weathering agencies, both chemical and mechanical, and their effects upon the color, strength, and durability of the various stones. The chemical tests used to determine the permanence of color and resistance to corrosion, together with the mechanical tests for determining the absorptive powers, resistance to freezing, resistance to abrasion, crushing strength, etc., are described at some length.

Summary Report of the Geological Survey Department for the Year 1896. By G. M. DAWSON. *Geol. Surv. Canada, Ann. Rep.*, 9, *Rep. A*, 3–144 (1898).—In addition to the accounts of the geological work, the report includes a general description of the work done in the chemical laboratory of the survey upon the waters, fuels, building stones, ores, etc., of Canada.

Report of the Section of Chemistry and Mineralogy. By G. CHRISTIAN HOFFMAN. *Geol. Surv. Canada, Ann. Rep.*, 9, *Rep. R*, 1–53 (1898).—The report includes a large number of analyses of coals, building stones, waters, and minerals, by F. G. Wait and R. A. A. Johnston. Of the minerals, the most noteworthy is that of baddeckite, a new copper-red variety of muscovite, corresponding to the formula

$$H_4(CaMgK_2Na_2)(Fe_2Al_2)_3Si_8O_{28}.$$

The results of some 87 gold and silver assays, and 5 nickel and cobalt assays by Mr. Johnston are also given.

APPARATUS.

A. H. GILL, REVIEWER.

An Apparatus to Facilitate Hydrogen Sulphide Precipitations. By R. K. MEADE. *J. Am. Chem. Soc.*, 21, 421.—The gas enters and exits through openings of capillary size, and the absorption is aided by shaking.

A Simple Volumenometer. By C. E. Linebarger. *J. Am. Chem. Soc.*, **21**, 435–437.—The apparatus resembles that of McKenna and possesses the additional advantage that it can be constructed of apparatus occurring in any laboratory.

The Incandescent Lamp as a Source of Heat in Ether Extraction. By C. G. Hopkins. *J. Am. Chem. Soc.*, **21**, 645–647.—Five 32-candle-power lamps furnish sufficient heat for twenty sets of Soxhlet extractors.

An Electric Drying Oven. By T. W. Richards. *Am. Chem. J.*, **22**, 45–49.—The oven itself consists of one large bottomless beaker inside another, both resting upon a tile, which is supported upon layers of asbestos and wire gauze. An inverted clock glass or porcelain dish serves as a cover. The source of heat is 5 m. of platinum wire, 0.2 mm. in diameter, wound upon a reel of glass rods and porcelain bars; a current of 2 amperes (potential of 52 volts) gives heat sufficient to heat the oven 140° above the temperature of the room. To equalize the temperature within the oven a face is placed immediately above the heating coil. The apparatus is safe, easily constructed, and very satisfactory.

A Serviceable Generator for Hydrogen Sulphide. By W. P. Bradley. *Am. Chem. J.*, **21**, 371–376.—The apparatus, which cannot well be understood without the figure, is easily constructed and cared for, and after an experience of nine years is said to leave little to be desired.

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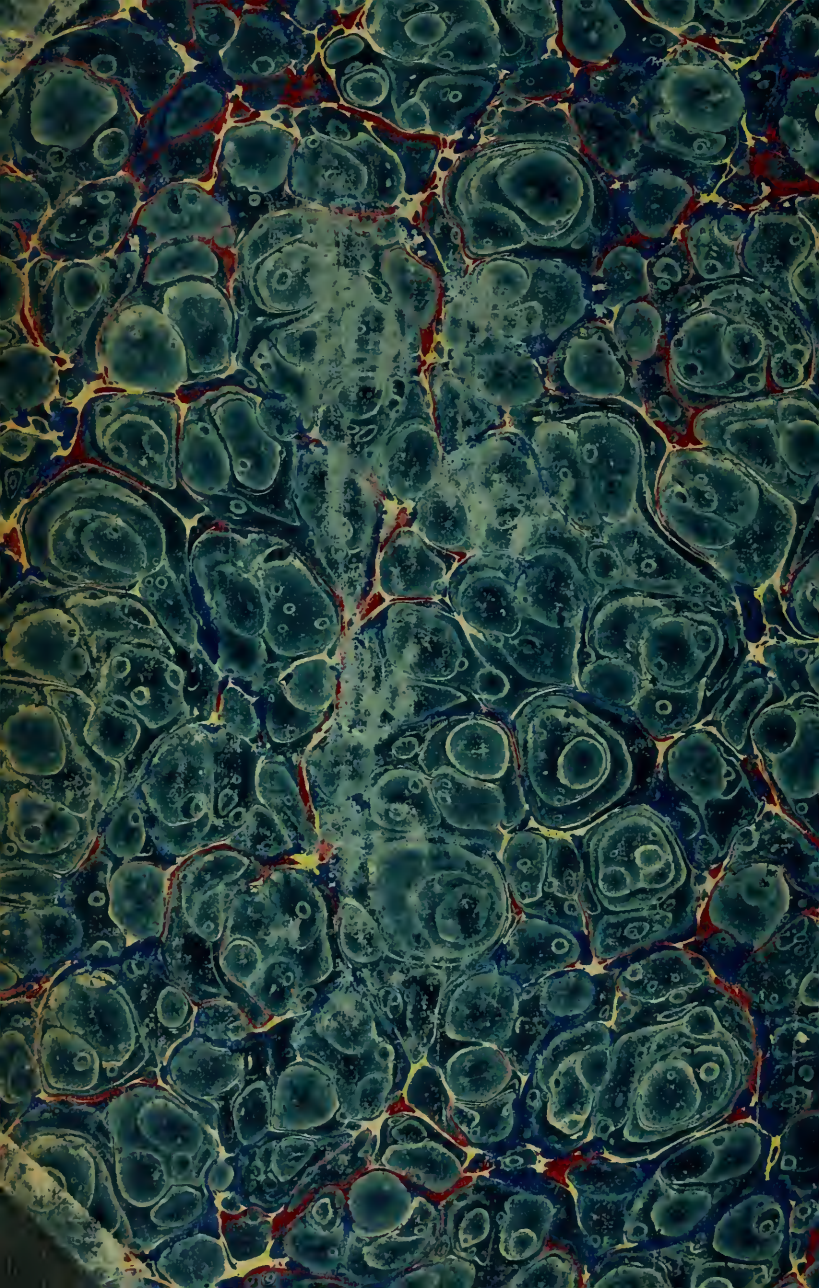
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